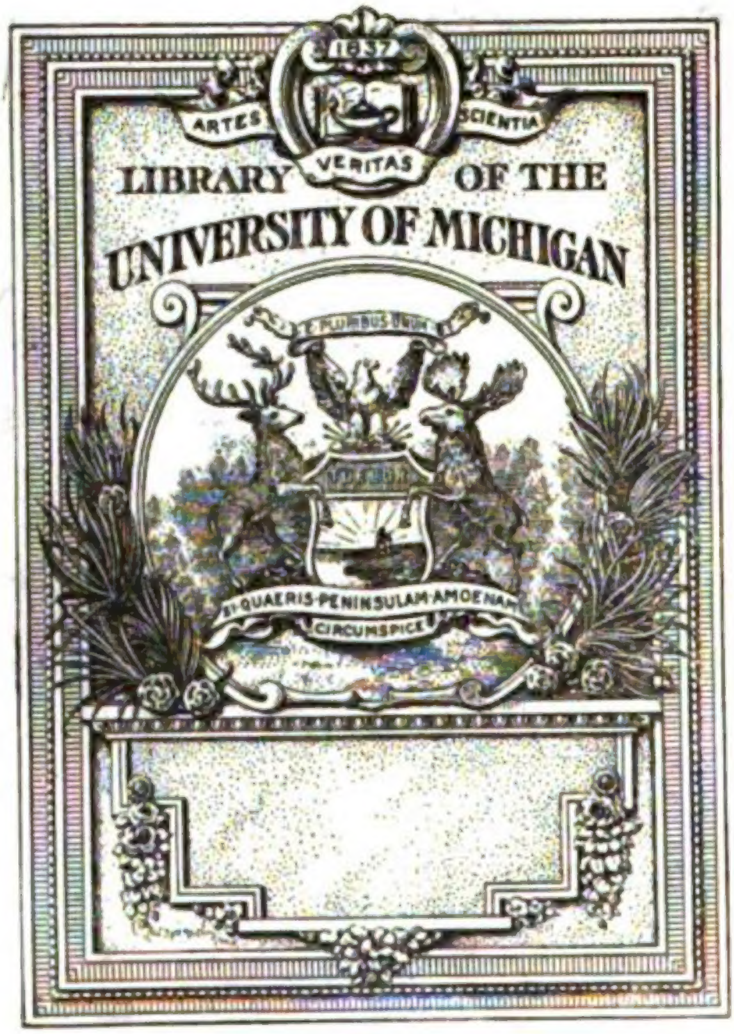
JOURNAL OF THE CHEMICAL SOCIETY


LIBRARY OF THE UNIVERSITY OF MICHIGAN

East
Libra

JOURNAL

OF

THE CHEMICAL SOCIETY.

TRANSACTIONS.

Committee of Publication:

E. C. C. Baly.
Horace T. Brown, LL.D., F.R.S.
A. W. Crossley, D.Sc., Ph.D., F.R.S.
Wyndham R. Dunstan, M.A., F.R.S.
M. O. Forster, D.Sc., Ph.D., F.R.S.
J. T. Hewitt, M.A., D.Sc., Ph.D.
R. Meldola, F.R.S.
G. T. Morgan, D.Sc.
Sir W. Ramsay, K.C.B., LL.D., F.R.S.
A. Scott, M.A., D.Sc., F.R.S.
T. E. Thorpe, C.B., LL.D., F.R.S.
John Wade, D.Sc.

Editor:
J. C. Cain, D.Sc., Ph.D.

Sub-Editor:
A. J. Greenaway.

Assistant Sub-Editor:
C. H. Desch, D.Sc., Ph.D.

1908. Vol. XCIII.

LONDON:
GURNEY & JACKSON, 10, PATERNOSTER ROW.
1908.

Richard Clay & Sons, Limited,
BREAD STREET HILL, E.C., AND
BUNGAY, SUFFOLK.

CONTENTS.

PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

PAGE

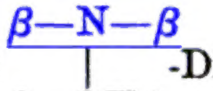
I.—The Relation between Unsaturation and Optical Activity. Part I. The Menthyl and Bornyl Esters of β-Phenylpropionic, Cinnamic, and Phenylpropiolic Acids. By Thomas Percy Hilditch 1

II.—Note on the Iodates and Periodates of the Alkali Metals and the Ammonium Radicle. By Thomas Vipond Barker, B.A., B.Sc. (Oxon.) 15

III.—Acylogens and Thiocarbamides. By Augustus Edward Dixon and John Taylor 18

IV.—Condensation of Ketones containing the Group $\cdot CH_2\cdot CO\cdot CH:$ with Esters in Presence of Sodium Ethoxide. By Reginald W. L. Clarke, Arthur Lapworth, and Elkan Wechsler . 30

V.—The Electrometric Determination of the Hydrolysis of Salts. By Henry George Denham, M.A., M.Sc., 1851 Exhibition Scholar, University of New Zealand 41

VI.—Attempted Synthesis of  $\begin{array}{l}\beta\text{—N—}\beta\\ \quad\ |\\ \beta\text{—CH}\beta\end{array}$ -Dinaphthacridines ; Condensation of Methylene Dichloride and 1-Substituted-2-naphthylamines. By Alfred Senier and Percy Corlett Austin 63

VII.—The Direct Interaction of Aryl Halides and Magnesium. By James Frederick Spencer and Eleanor Marguerite Stokes 68

VIII.—The Triazo-Group. Part I. Triazoacetic Acid and Triazoacetone (Acetonylazoimide). By Martin Onslow Forster and Hans Eduard Fierz 72

IX.—The Influence of Acids and Alkalis on the Velocity of Formation of Acetoxime. By Ernest Barrett and Arthur Lapworth 85

X.—A Colorimetric Method for the Determination of Small Percentages of Iron in Copper Alloys. By Arnold William Gregory, B.Sc. (Lond.) 93

XI—Derivatives of Tetramethyl Glucose. By James Colquhoun Irvine, D.Sc., Ph.D., and Agnes Marion Moodie, M.A., B.Sc. (Carnegie Scholar) 95

196006

PAGE

XII.—Studies of Dynamic Isomerism. Part VI. The Influence of Impurities on the Mutarotation of Nitrocamphor. By T. MARTIN LOWRY and EGBERT H. MAGSON 107

XIII.—Studies of Dynamic Isomerism. Part VII. Note on the Action of Carbonyl Chloride as an Agent for Arresting Isomeric Change. By T. MARTIN LOWRY and EGBERT H. MAGSON 119

XIV.—The Effect on Heat on the Alkyl Iodides. By ZELDA KAHAN, B.Sc. 132

XV.—Derivatives of *S*-Phenylphenazothionium. Part I. By SAMUEL SMILES and THOMAS PERCY HILDITCH 145

XVI.—The Velocity of Reduction of the Oxides of Lead, Cadium, and Bismuth by Carbon Monoxide, and the Existence of the Suboxides of these Metals. By FRANCIS JOSEPH BRISLEE, D.Sc. 154

XVII.—The Formation and Reactions of Imino-Compounds. Part VI. The Formation of Derivatives of Hydrindene from *o*-Phenylenediacetonitrile. By CHARLES WATSON MOORE and JOCELYN FIELD THORPE 165

XVIII.—The Colour of Cupric Salts in Aqueous Solution. By NEVIL VINCENT SIDGWICK and HENRY THOMAS TIZARD . 187

XIX.—Organic Derivatives of Silicon. Part IV. The Sulphonation of Benzylethylpropylsilicyl Oxide and of Benzylethyldipropylsilicane. By HERBERT MARSDEN, B.Sc. (Vict.), and FREDERIC STANLEY KIPPING 198

XX.—The Esterification Constants of the Normal Fatty Acids. By JOHN JOSEPH SUDBOROUGH and JAMES MYLAM GITTINS . 210

XXI.—Studies in Fermentation. Part II. The Mechanism of Alcoholic Fermentation. By ARTHUR SLATOR, Ph.D., D.Sc. 217

XXII.—Studies in the Camphane Series. Part XXV. Action of Diazomethane on the Two Modifications of *iso*Nitrosocamphor. By MARTIN ONSLOW FORSTER and HENRY HOLMES 242

XXIII.—The Constitution of Umbellulone. Part III. By FRANK TUTIN 252

XXIV.—Valency. By JOHN ALBERT NEWTON FRIEND, Ph.D. . 260

XXV.—The Oxidation of Aromatic Hydrazines by Metallic Oxides, Permanganates, and Chromates. By FREDERICK DANIEL CHATTAWAY 270

XXVI.—The Reaction between Calcium Carbonate and Chlorine Water. By ARTHUR RICHARDSON, Ph.D. 280

XXVII.—Contributions to the Chemistry of the Terpenes. Part III. Some Oxidation Products of Pinene. By GEORGE GERALD HENDERSON and ISIDORE MORRIS HEILBRON . . 288

XXVIII.—The Effect of Constitution on the Rotatory Power of Optically Active Ammonium Compounds. Part II. By HUMPHREY OWEN JONES and JOHN ROBERTSHAW HILL . . 295

PAGE

XXIX.—The Preparation of *l*-Benzoin. By ALEX. MCKENZIE and HENRY WREN 309

XXX.—The Bromination of *p*-Hydroxydiphenylamine. By ALICE EMILY SMITH and KENNEDY JOSEPH PREVITÉ ORTON . 314

XXXI.—The Reducibility of Magnesium Oxide by Carbon. By ROLAND EDGAR SLADE, M.Sc. 327

XXXII.—Constitution and Colour of Azo-compounds. Part II. The Salts of Para-hydroxyazo-compounds with Acids. By JOHN JACOB FOX and JOHN THEODORE HEWITT . . 333

XXXIII.—The Influence of Foreign Substances on Transition Temperatures and the Determination of Molecular Weights. By HARRY MEDFORTH DAWSON and COLIN GYRTH JACKSON . 344

XXXIV.—Malacone, a Silicate of Zirconium. By ALEXANDER CHARLES CUMMING, D.Sc. 350

XXXV.—The Influence of Solvents on the Rotation of Optically Active Compounds. Part XI. Ethyl Tartrate in Aliphatic Halogen Derivatives. By THOMAS STEWART PATTERSON and DAVID THOMSON, M.A., B.Sc. (late Carnegie Research Scholar) 355

XXXVI.—The Refractive Power of Diphenylhexatriene and Allied Hydrocarbons. By IDA SMEDLEY 372

XXXVII.—The Temperatures of Spontaneous Crystallisation of Mixed Solutions and their Determination by Means of the Index of Refraction. Mixtures of Solutions of Sodium Nitrate and Lead Nitrate. By FLORENCE ISAAC, Research Fellow of Somerville College 384

XXXVIII.—Amphoteric Metallic Hydroxides. Part I. By JOHN KERFOOT WOOD 411

XXXIX.—Anomalous Behaviour of the Hydrogen-Electrode in Solutions of Lead Salts, and the Existence of Univalent Lead Ions in Aqueous Solutions. By HENRY GEORGE DENHAM, M.A., M.Sc., and ARTHUR JOHN ALLMAND, M.Sc. . 424

XL.—The Preparation of Conductivity Water. By HAROLD HARTLEY, NORMAN PHILLIPS CAMPBELL, and REGINALD HOLLIDAY POOLE 428

XLI.—The Formation of 4-Pyrone Compounds from Acetylenic Acids. Part I. By SIEGFRIED RUHEMANN 431

XLII.—Researches on the Anthraquinones. By WILLIAM HENRY BENTLEY and CHARLES WEIZMANN 435

XLIII.—Organic Derivatives of Silicon. Part V. Benzylethylsilicone, Dibenzylsilicon, and other Benzyl and Benzylethyl Derivatives of Silicane. By ROBERT ROBISON, B.Sc., and FREDERIC STANLEY KIPPING 439

XLIV.—Organic Derivatives of Silicon. Part VI. The Optically Active Sulphobenzylethylpropylsilicyl Oxides. By FREDERIC STANLEY KIPPING 457

PAGE

XLV.—The Metallic Picrates. By Oswald Silberrad, Ph.D., and Henry Ablett Phillips 474

XLVI.—Brazilin and Hæmatoxylin. Part VIII. Synthesis of Brazilinic Acid, the Lactones of Dihydrobrazilinic and Dihydrohæmatoxylinic Acids, Anhydrobrazilic Acid, &c. The Constitution of Brazilin, Hæmatoxylin, and their Derivatives. By William Henry Perkin, jun., and Robert Robinson 489

XLVII.—The Crystal Form of Halogen Derivatives of Open-chain Hydrocarbons with Reference to the Barlow-Pope Theory of Structure. By Frans Maurits Jaeger, Ph.D. . 517

XLVIII.—The Residual Affinity of the Coumarins and Thiocoumarins as shown by their Additive Compounds. By Arthur Clayton, B.Sc. 524

XLIX.—Colour and Constitution of Azomethine Compounds. Part I. By Frank George Pope 532

L.—Some Physico-Chemical Properties of Mixtures of Pyridine and Water. By Harold Hartley, Noel Garrod Thomas, and Malcolm Percival Applebey 538

LI.—The Viscosity of Aqueous Pyridine Solutions By Albert Ernest Dunstan and Ferdinand Bernard Thole . . 561

LII.—The Action of Thionyl Chloride and of Phosphorus Pentachloride on the Methylene Ethers of Catechol Derivatives. By George Barger 563

LIII.—Experiments on the Synthesis of the Terpenes. Part XII. Synthesis of Terpins, Terpineols, and Trepenes derived from Methyl*iso*propyl*cyclo*pentanes, $Me\cdot C_5H_8\cdot CHMe_2$. By Walter Norman Haworth and William Henry Perkin, jun. 573

LIV.—A β-Lactonic Acid from Acetone and Malonic Acid. By Andrew Norman Meldrum (Carnegie Research Fellow) . 598

LV.—Derivatives of para-Diazoiminobenzene. By Gilbert T. Morgan and Frances M. G. Micklethwait . . . 602

LVI.—A Study of the Diazo-reaction in the Diphenyl Series. By Gilbert T. Morgan and Frances M. G. Micklethwait 614

LVII.—The Action of Mustard Oils on the Ethyl Esters of Malonic and Cyanoacetic Acids. By Siegfried Ruhemann 621

LVIII.—Substituted Dihydrobenzenes. Part II. 1:1-Dimethyl-$\Delta^{2:4}$-dihydrobenzene and 1:1 Dimethyl-$\Delta^{2:5}$-dihydrobenzene. By Arthur William Crossley and Nora Renouf, Salters' Research Fellow 629

LIX.—The Affinity Constants of Bases as Determined by the Aid of Methyl-orange. By Victor Herbert Veley . . 652

LX.—Traces of a New Tin-group Element in Thorianite. By Clare de Brereton Evans 667

PAGE

LXI.—The Triazo-Group. Part II. Azoimides of Propionic Ester and of Methyl Ethyl Ketone. By MARTIN ONSLOW FORSTER and HANS EDUARD FIERZ 669

LXII.—A New Form of Pyknometer. By WILLIAM ROBERT BOUSFIELD, M.A., K.C. 679

LXIII.—Para- and Meta-nitrosoacetanilide. By JOHN CANNELL CAIN 681

LXIV.—The Constitution of "Thiocyanates" containing an Electronegative Group. By AUGUSTUS E. DIXON and JOHN TAYLOR 684

LXV.—The Relation between Unsaturation and Optical Activity. Part II. Alkaloid Salts of Corresponding Saturated and Unsaturated Acids. By THOMAS PERCY HILDITCH . . . 700

LXVI.—The Action of Heat on α-Hydroxycarboxylic Acids. Part IV. Racemic αα′-Dihydroxyadipic Acid and meso-αα′-Dihydroxyadipic Acid. By HENRY RONDEL LE SUEUR . 716

LXVII.—The Wandering of Bromine in the Transformation of Nitroaminobromobenzenes. By KENNEDY JOSEPH PREVITÉ ORTON and CONSTANCE PEARSON 725

LXVIII.—The Action of Thionyl Chloride on the Methylene Ethers of Catechol Derivatives. Part II. Piperonyloin, Piperil, and Hydropiperoin. By GEORGE BARGER and ARTHUR JAMES EWINS 735

LXIX.—The Solubility of Iodine in Water. By HAROLD HARTLEY and NORMAN PHILLIPS CAMPBELL 741

LXX.—The Sulphination of Phenolic Ethers and the Influence of Substituents. By SAMUEL SMILES and ROBERT LE ROSSIGNOL 745

ANNUAL GENERAL MEETING 763

PRESIDENTIAL ADDRESS 774

LXXI.—Orthobromophenols and Some Bromonitrophenols. By PHILIP WILFRED ROBERTSON 788

LXXII.—The Optical Activity of Compounds having Simple Molecular Structure. By WILLIAM JACKSON POPE and JOHN READ 794

LXXIII.—The Action of Potassium Sulphide on Potassium Tetrathionate in Aqueous Solution. By ARTHUR COLEFAX, M.A., Barrister-at-Law 798

LXXIV.—The Displacement of Halogen in 1-Phenylchloroacetic Acid by Hydroxy- and Methoxy-groups. A Contribution to the Chemistry of the Walden Inversion. By ALEX. McKENZIE and GEORGE WILLIAM CLOUGH 811

LXXV.—The Spontaneous Crystallisation of Sodium Sulphate Solutions. By HAROLD HARTLEY, BERNARD MOUAT JONES, and GEORGE ADRIAN HUTCHINSON 825

PAGE

LXXVI.—The Existence in Aqueous Solutions of a Univalent Cadmium Ion, a Subvalent Thallium Ion, and a Bivalent Bismuth Ion. By HENRY GEORGE DENHAM, M.A., M.Sc., 1851 Exhibition Scholar, University of New Zealand . 833

LXXVII.—The Condensation of Epichlorohydrin with Phenols. By DAVID RUNCIMAN BOYD and ERNEST ROBERT MARLE . 838

LXXVIII.—Constitution of Hydroxyazo-compounds. Action of Diazomethane and of Mercuric Acetate. By CLARENCE SMITH [and, in part, ALEC DUNCAN MITCHELL] 842

LXXIX.—The Quantitative Conversion of Aromatic Hydrazines into Diazonium Salts. By FREDERICK DANIEL CHATTAWAY 852

LXXX.—Quantitative Separation of Thallium from Silver. By JAMES FREDERICK SPENCER and MARGARET LE PLA . . 858

LXXXI.—The Constituents of Cyprus Organum Oil. Isolation of a New Terpene (Origanene). By SAMUEL SHROWDER PICKLES, M.Sc. 862

LXXXII.—The Molecular Complexity of Amides in Various Solvents. By ANDREW NORMAN MELDRUM and WILLIAM ERNEST STEPHEN TURNER 876

LXXXIII.—The Constituents of Olive Leaves. By FREDERICK BELDING POWER and FRANK TUTIN 891

LXXXIV.—The Constituents of Olive Bark. By FREDERICK BELDING POWER and FRANK TUTIN 904

LXXXV.—The Refraction and Dispersion of Triazo-compounds. By JAMES CHARLES PHILIP 918

LXXXVI.—The Dissociation Constants of Triazoacetic and α-Triazopropionic Acids. By JAMES CHARLES PHILIP . . 925

LXXXVII.—The Spontaneous Crystallisation of Substances which form a Continuous Series of Mixed Crystals. Mixture of Naphthalene and β-Naphthol. By HENRY A. MIERS, F.R.S., and FLORENCE ISAAC 927

LXXXVIII.—The Influence of Solvents on the Rotation of Optically Active Compounds. Part XII. Ethyl Tartrate in Aromatic Halogen Derivatives. By THOMAS STEWART PATTERSON and DAVID PATERSON MCDONALD, M.A., B.Sc. . 936

LXXXIX.—Acetylketen: a Polymeride of Keten. By FRANCES CHICK and NORMAN THOMAS MORTIMER WILSMORE . . 946

XC.—The Condensation of Benzoin with Methyl Alcohol. By JAMES COLQUHOUN IRVINE, D.Sc., Ph.D., and DAVID MCNICOLL, M.A., B.Sc. 950

XCI.—A New General Method of Preparing Diazonium Bromides. By FREDERICK DANIEL CHATTAWAY . . . 958

XCII.—The Absorption Spectrum of Camphor. By WALTER NOEL HARTLEY, D.Sc., F.R.S. 961

PAGE

XCIII.—The Chemical Action of Radium Emanation. Part III. On Water and Certain Gases. By ALEXANDER THOMAS CAMERON and SIR WILLIAM RAMSAY, K.C.B. 966

XCIV.—The Chemical Action of Radium Emanation. Part IV. On Water. By ALEXANDER THOMAS CAMERON and SIR WILLIAM RAMSAY, K.C.B. 992

XCV.—Molecular Volumes of the Nitrites of Silver, Mercury, and the Alkali Metals. By PRAFULLA CHANDRA RÂY . 997

XCVI.—The Mutual Solubility of 2-Methylpiperidine and Water. By OTTO FLASCHNER and BASIL MACEWEN . . 1000

XCVII.—The Viscosity of Solutions. By CHARLES EDWARD FAWSITT 1004

XCVIII.—A Criticism of Werner's Theory and the Constitution of Complex Salts. By JOHN ALBERT NEWTON FRIEND, Ph.D. 1006

XCIX.—The Reaction of Diazonium Salts with Mono- and Di-hydric Phenols and with Naphthols. By KENNEDY JOSEPH PREVITÉ ORTON and REGINALD WILLIAM EVERATT . 1010

C.—Ethyl 6-Methyl-2-pyrone-3:5-dicarboxylate and its Derivatives. By JOHN LIONEL SIMONSEN 1022

CI.—The Melting Points of the Anilides, *p*-Toluidides, and *a*-Naphthalides of the Normal Fatty Acids. By PHILIP WILFRED ROBERTSON 1033

CII.—The Volumetric Estimation of Silver. By WILLIAM ROBERT LANG and JOHN OBINS WOODHOUSE . . . 1037

CIII.—The Polarimetric Study of Intramolecular Rearrangement in Inactive Substances. By THOMAS STEWART PATTERSON and ANDREW MCMILLAN, M.A., B.Sc. (Carnegie Research Fellow) 1041

CIV.—Contributions to the Chemistry of the Amidines. Part II. Anilinobenzoxazole and the Supposed Anilodihydrobenzoxazole. By GEORGE YOUNG and ALBERT EDWARD DUNSTAN 1052

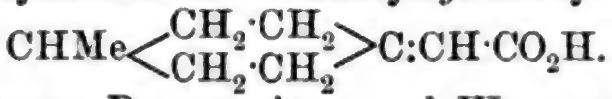
CV.—The Relation between Dielectric Constant and Chemical Constitution. Part I. Stereoisomeric Compounds. By ALFRED WALTER STEWART (Carnegie Research Fellow) . 1059

CVI.—An Apparatus for Determining the Specific Inductive Capacity of Organic Liquids. By ALFRED WALTER STEWART (Carnegie Research Fellow) 1062

CVII.—Titani-dihydroxymaleic Acid, and the Detection of Titanium. By HENRY JOHN HORSTMAN FENTON . . 1064

CVIII.—The Triazo-group. Part III. Bistriazo-derivatives of Ethane and of Acetic Ester. By MARTIN ONSLOW FORSTER, HANS EDUARD FIERZ, and WALTER PHILIP JOSHUA . . 1070

PAGE

CIX.—Experiments on the Synthesis of 1-Methyl*cyclo*hexylidene-4-acetic Acid,  $CHMe<\genfrac{}{}{0pt}{}{CH_2{\cdot}CH_2}{CH_2{\cdot}CH_2}>C{:}CH{\cdot}CO_2H$. Part I. By William Henry Perkin, jun., and William Jackson Pope 1075

CX.—The Synthesis and Constitution of Certain Pyranol Salts Related to Brazilein and Hæmatein. By William Henry Perkin, jun., Robert Robinson, and (in part) Maurice Russell Turner 1085

CXI.—Brazilin, Hæmatoxylin, and their Derivatives. Part IX. On Brazilein, Hæmatein, and their Derivatives. By Paul Engels, William Henry Perkin, jun., and Robert Robinson 1115

CXII.—The Interaction of Copper and Nitric Acid in Presence of Metallic Nitrates Considered with Reference to the Existence of Hydrates in Solution. By Edward Henry Rennie, M.A., D.Sc., Alfred J. Higgin, F.I.C., and William Ternent Cooke, D.Sc. 1162

CXIII.—Condensation Products from Aminopinenedicarboxylic Acid. By William Godden, B.Sc. 1171

CXIV.—The Triazo-group. Part IV. Allylazoimide. By Martin Onslow Forster and Hans Eduard Fierz . . 1174

CXV.—Aromatic Arsonic and Arsinic Acids. By Frank Lee Pyman and William Colebrook Reynolds . . . 1180

CXVI.—The Electrolytic Oxidation of Some Hydroxybenzoic Acids. By Arthur George Perkin and Frederick Mollwo Perkin 1186

CXVII.—The Thermal Decomposition of Hydrocarbons. Part I. [Methane, Ethane, Ethylene, and Acetylene.] By William Arthur Bone and Hubert Frank Coward 1197

CXVIII.—The Effect of Constitution on the Optical Activity of Nitrogen Compounds. By Reginald William Everatt, B.Sc. 1225

CXIX.—Acids as Accelerators in the Acetylation of the Amino-groups. By Alice Emily Smith and Kennedy Joseph Previté Orton 1242

CXX.—The Hydrolysis of Amygdalin by Emulsin. Part I. By S. J. Manson Auld, Ph.D. 1251

CXXI.—The Hydrolysis of Amygdalin by Emulsin. Part II. By S. J. Manson Auld, Ph.D. 1276

CXXII.—The Formation of 4-Pyrone Compounds from Acetylenic Acids. Part II. By Siegfried Ruhemann . . 1281

CXXIII.—α-Methylcamphor and Fenchone. By Walter Hamis Glover 1285

CXXIV.—Viscosity Determinations at High Temperatures. By Charles Edward Fawsitt 1299

PAGE

CXXV.—The Formation of Polyiodides in Nitrobenzene Solution. Part III. The Chemical Dissociation of the Polyiodides of the Alkali Metals and Ammonium Radicles. By HARRY MEDFORTH DAWSON 1308

CXXVI.—The Study of the Absorption Spectra of the Hydrocarbons Isolated from the Products of the Action of Aluminium Chloride on Naphthalene. By ANNIE HOMER, Fellow of Newnham College, and JOHN EDWARD PURVIS, M.A. 1319

CXXVII.—Cholestenone. By CHARLES DORÉE and JOHN ADDYMAN GARDNER 1328

CXXVIII.—Apparatus for Experiments at High Temperatures and Pressures, and its Application to the Study of Carbon. By RICHARD THRELFALL, F.R.S. 1333

CXXIX.—The Rusting of Iron. By WILLIAM AUGUSTUS TILDEN 1356

CXXX.—Some Esters of Arsenious Acid. By WILLIAM ROBERT LANG, JOHN FRANCIS MACKEY, and ROSS AITKEN GORTNER 1364

CXXXI.—Benzeneazo-2-pyridone. By WILLIAM HOBSON MILLS and SIBYL T. WIDDOWS 1372

CXXXII.—Aromatic Selenonium Bases. By THOMAS PERCY HILDITCH and SAMUEL SMILES 1384

CXXXIII.—The Relation between Unsaturation and Optical Activity. Part III. Optically Active Salts of Acids Containing Adjacent Unsaturated Groups. By THOMAS PERCY HILDITCH 1388

CXXXIV.—The Preparation of Disulphides. Part II. The Action of Alkalis on Sodium Alkyl Thiosulphates. By THOMAS SLATER PRICE and DOUGLAS FRANK TWISS . . 1395

CXXXV.—The Preparation of Disulphides Part III. The Nitrobenzyl Disulphides. By THOMAS SLATER PRICE and DOUGLAS FRANK TWISS 1401

CXXXVI.—Solubility of Silver Chloride in Mercuric Nitrate Solution. By BERTRAM HAWARD BUTTLE and JOHN THEODORE HEWITT 1405

CXXXVII.—The *cis*- and *trans*-Modifications of 1-Methyl*cyclo*hexan-2-ol-4-carboxylic Acid and their Conversion into 1-Methyl-Δ^1-*cyclo*hexene-4-carboxylic Acid. By ANDREW NORMAN MELDRUM (Carnegie Research Fellow) and WILLIAM HENRY PERKIN, jun. 1416

CXXXVIII.—The Constitution of Glucose Derivatives. Part I. Glucose-anilide, -oxime, and -hydrazone. By JAMES COLQUHOUN IRVINE, Ph.D., D.Sc., and ROBERT GILMOUR . 1429

CXXXIX.—The Use of the Micro-balance for the Determinations of Electrochemical Equivalents and for the Measurement of Densities of Solids. By OTTO BRILL and CLARE DE BRERETON EVANS 1442

d by Google

PAGE

CXL.—The Fluorescence of Platinocyanides. By LEONARD ANGELO LEVY 1446

CXLI.—The Reduction of Aromatic Nitro-compounds to Azoxy-derivatives in Acid Solution. By BERNHARD FLÜRSCHEIM and THEODOR SIMON 1463

CXLII.—The Reduction of Refractory Oxides by Carbon. By HAROLD CECIL GREENWOOD, M.Sc. 1483

CXLIII.—The Production of Ferro-alloys. By HAROLD CECIL GREENWOOD, M.Sc. 1496

CXLIV.—The Proteins of Egg-yolk. By R. H. ADERS PLIMMER, D.Sc. 1500

CXLV.—The Action of Bromine on β-Hydrindone. By NORMAN ALLEN CREETH and JOCELYN FIELD THORPE 1507

CXLVI.—The Constituents of Canadian Hemp. Part I. Apocynin. By HORACE FINNEMORE, B.Sc. 1513

CXLVII.—A New Synthesis of Apocynin. By HORACE FINNEMORE, B.Sc. 1520

CXLVIII.—Aromatic α-Disulphones. By THOMAS PERCY HILDITCH 1524

CXLIX.—On Polymorphism, with Especial Reference to Sodium Nitrate and Calcium Carbonate. By WILLIAM BARLOW and WILLIAM JACKSON POPE 1528

CL.—The Action of Nitrous Gases on Di*cyclo*pentadiene. By ALEXANDER RULE 1560

CLI.—The Constitution of Co-ordinated Compounds. By SAMUEL HENRY CLIFFORD BRIGGS 1564

CLII.—The Rapid Electroanalytical Deposition and Separation of Metals. Part II. Antimony and Tin. The Employment of a Diaphragm. By HENRY JULIUS SALOMON SAND . . 1572

CLIII.—The Electrolytic Chlorination of the Salts of Organic Acids. By JOHN KENNETH HAROLD INGLIS and FRED WOOTTON 1592

CLIV.—The Conductivities of the α-Oximino-fatty Acids. By JOHN KENNETH HAROLD INGLIS and LOTTIE EMILY KNIGHT . 1595

CLV.—The Formation of Ethers from Compounds of the Benzoin Type. By JAMES COLQUHOUN IRVINE, Ph.D., D.Sc., and DAVID MCNICOLL, M.A., B.Sc. (Carnegie Scholar) . . 1601

CLVI.—Studies of the Perhalogen Salts. Part II. By CHARLES KENNETH TINKLER 1611

CLVII.—The Relation between Unsaturation and Optical Activity. Part IV. The Relative Influence of Bi-, Quadri-, and Sexa-valent Sulphur on Rotatory Power. By THOMAS PERCY HILDITCH 1618

CLVIII.—Coprosterol. Part I. By CHARLES DORÉE and JOHN ADDYMAN GARDNER 1625

PAGE

CLIX.—Oxidation of Hydrocarbons of the Benzene Series. Part II. Substances containing a Negative Radicle. By HERBERT DRAKE LAW and FREDERICK MOLLWO PERKIN . 1633

CLX.—The Measurement of a Homogeneous Chemical Change in a Gas. (The Thermal Decomposition of Ozone.) By HERBERT EDMUND CLARKE and DAVID LEONARD CHAPMAN . 1638

CLXI.—The Preparation of Disulphides. Part IV. Esters of Dithiodiglycollic and Dithiodilactylic Acids. By THOMAS SLATER PRICE and DOUGLAS FRANK TWISS 1645

CLXII.—The Constituents of the Expressed Oil of Nutmeg. By FREDERICK BELDING POWER and ARTHUR HENRY SALWAY . 1653

CLXIII.—Syntheses with Phenol Derivatives containing a Mobile Nitro-group. Part I. The Interaction of 2:3:5-Trinitro-4-acetylaminophenol and Amines. By RAPHAEL MELDOLA, F.R.S., and JAMES GORDON HAY 1659

CLXIV.—Contributions to the Chemistry of the Cholesterol Group. Part I. The Action of Hydrogen Peroxide and of Fused Potassium Hydroxide on Cholesterol. By ROBERT HOWSON PICKARD and JOSEPH YATES 1678

CLXV.—Derivatives of *S*-Phenylphenazothionium. Part II. By SAMUEL SMILES and THOMAS PERCY HILDITCH 1687

CLXVI.—A Reaction Distinguishing Phosphoprotein from Nucleoprotein and the Distribution of Phosphoproteins in Tissues. By R. H. ADERS PLIMMER and F. H. SCOTT . . 1699

CLXVII.—The Colouring Matters of the Stilbene Group. Part V. The Action of Caustic Alkalis on Derivatives of para-Nitrotoluene. By ARTHUR GEORGE GREEN and JAMES BADDILEY . 1721

CLXVIII.—The Trithionates and Tetrathionates of the Alkali Metals. Part I. By JOHN EDWIN MACKENZIE (Research Fellow of the University of Edinburgh) and HUGH MARSHALL 1726

CLXIX.—The Spontaneous Crystallisation of Solutions of some Alkali Nitrates. By BERNARD MOUAT JONES 1739

CLXX.—The Relation between Absorption Spectra and Chemical Constitution. Part IX. The Nitroso- and Nitro-groups. By EDWARD CHARLES CYRIL BALY and CECIL HENRY DESCH . 1747

CLXXI.—The Synthesis of Complex Acridines. By PERCY CORLETT AUSTIN 1760

CLXXII.—The Solubility of Lime in Water. By GERALD TATTERSALL MOODY and LEWIS THOMAS LEYSON 1767

CLXXIII.—The Chlorination of para-Nitroaniline. By BERNHARD FLÜRSCHEIM 1772

CLXXIV.—The Direct Action of Radium on Copper and Gold. By EDGAR PHILIP PERMAN 1775

CLXXV.—Syntheses with the Aid of Monochloromethyl Ether. Part I. The Action of Monochloromethyl Ether on the Sodium Derivatives of Ethyl Malonate and Ethyl *iso*Propylmalonate. By JOHN LIONEL SIMONSEN 1777

PAGE

CLXXVI.—The Effect of Constitution on the Rotatory Power of Optically Active Nitrogen Compounds. Part III. By Reginald William Everatt and Humphrey Owen Jones . 1789

CLXXVII.—Relation between Chemical Constitution and Physiological Action in Certain Substituted Aminoalkyl Esters. By Frank Lee Pyman 1793

CLXXVIII.—The Relation between Absorption Spectra and Chemical Constitution. Part X. Unsaturated Acids of the Benzene Series. By Edward Charles Cyril Baly and Konrad Schaefer 1808

CLXXIX.—The Relation between Viscosity and Chemical Constitution. Part II. The Existence of Racemic Compounds in the Liquid State. By Albert Ernest Dunstan and Ferdinand Bernard Thole 1815

CLXXX.—The Direct Interaction of Magnesium and Alkyl Halides. By James Frederick Spencer and Mary S. Crewdson 1821

CLXXXI.—The Interaction of Metals of the Aluminium Group and Organic Halogen Derivatives. By James Frederick Spencer and Marion L. Wallace 1827

CLXXXII.—The Interaction of Hydrogen Dioxide and Sulphides. By Maud Gazdar and Samuel Smiles 1833

CLXXXIII.—The Influence of Solvents on the Rotation of Optically Active Compounds. Part XIII. Ethyl Tartrate in Aromatic Nitro-derivatives. Influence of Temperature-change on Rotation in Solution. By Thomas Stewart Patterson 1836

CLXXXIV.—A New Form of Gas Burette. By Arthur Edwin Hill 1857

CLXXXV.—The Triazo-group. Part V. Resolution of a-Triazopropionic Acid. By Martin Onslow Forster and Hans Eduard Fierz 1859

CLXXXVI.—The Triazo-group. Part VI. Triazoethyl Alcohol and Triazoacetaldehyde. By Martin Onslow Forster and Hans Eduard Fierz 1865

CLXXXVII.—Experiments on the Synthesis of the Terpenes. Part I (continued). Resolution of *dl*-1-Methyl-Δ^1-*cyclo*hexene-4-carboxylic Acid and Synthesis of the Optically Active Modifications of Terpineol. By Kenneth Fisher and William Henry Perkin, jun. 1871

CLXXXVIII.—Experiments on the Synthesis of the Terpenes. Part XIII. Synthesis of *iso*Carvestrene ($\Delta^{6:8(9)}$-*m*-Menthadiene) and its Derivatives. By Kenneth Fisher and William Henry Perkin, jun. 1876

CLXXXIX.—Aromatic Arsonic Acids. By Marmaduke Barrowcliff, Frank Lee Pyman, and Frederic George Percy Remfry 1893

d by Google

PAGE

CXC.—The Relation between Absorption Spectra and Chemical Constitution. Part XI. Some Aromatic Hydrocarbons. By EDWARD CHARLES CYRIL BALY and WILLIAM BRADSHAW TUCK 1902

CXCI.—Colour and Constitution of Azomethine Compounds. Part II. By FRANK GEO. POPE and ROBERT FLEMING . . 1914

CXCII.—The Relation between Viscosity and Chemical Constitution. Part III. The Enol-ketonic Tautomerism. By ALBERT ERNEST DUNSTAN and JAMES ARTHUR STUBBS . . 1919

CXCIII.—Contributions to the Chemistry of the Cholesterol Group. Part II. Some Oxidation Products of Sitosterol. By ROBERT HOWSON PICKARD and JOSEPH YATES . . . 1928

CXCIV.—The Condensation of Salicylaldehyde and Benzamide. By ARTHUR WALSH TITHERLEY and MORRIS EDGAR MARPLES. 1933

CXCV.—Experiments on the Synthesis of 1-Methyl*cyclo*hexylidene-4-acetic Acid. Part II. By VICTOR JOHN HARDING, WALTER NORMAN HAWORTH, and WILLIAM HENRY PERKIN, jun. 1943

CXCVI.—The Direct Union of Carbon and Hydrogen. Synthesis of Methane. By WILLIAM ARTHUR BONE and HUBERT FRANK COWARD 1975

CXCVII.—The Chlorination of Methyl Derivatives of Pyridine. 2-Methylpyridine. Part II. By WILLIAM JAMES SELL . 1993

CXCVIII.—The Chlorine Derivatives of Pyridine. Part IX. Preparation and Orientation of 3:5-Dichloropyridine. By WILLIAM JAMES SELL 1997

CXCIX.—The Chlorine Derivatives of Pyridine. Part X. Orientation of 2:3:5-Trichloropyridine. By WILLIAM JAMES SELL 2001

CC.—Organic Derivatives of Silicon. Part VII. The Synthesis of *dl*-Sulphobenzylethyl*iso*butylsilicyl Oxide. By BERNARD DUNSTAN WILKINSON LUFF, A.I.C. (1851 Exhibition Scholar), and FREDERIC STANLEY KIPPING 2004

CCI.—The Coumarin Condensation. By ARTHUR CLAYTON . 2016

CCII.—Studies on the Viscosity and Conductivity of Some Aqueous Solutions. Part I. Solutions of Sucrose, Hydrogen Chloride, and Lithium Chloride. By W. HEBER GREEN, D.Sc. 2023

CCIII.—Studies on the Viscosity and Conductivity of Some Aqueous Solutions. Part II. Mixtures of Solutions of Sucrose and Lithium Chloride. A Contribution towards the Elucidation of the Connexion between Ionic Mobility and the Fluidity of the Solution. By W. HEBER GREEN, D.Sc. 2049

CCIV.—The Formation of Polyiodides in Nitrobenzene Solution. Part IV. The Electrolytic Dissociation of the Polyiodides of the Alkali Metals and Ammonium Radicles. By HARRY MEDFORTH DAWSON and COLIN GYRTH JACKSON . . . 2063

CCV.—Meteloidine: A New Solanaceous Alkaloid. By FRANK LEE PYMAN and WILLIAM COLEBROOK REYNOLDS . . . 2077

PAGE

CCVI.—The Action of Phosphorus Pentachloride on the Methylene Ethers of Catechol Derivatives. Part III. The Cyclic Carbonates of Dichloro-ethyl- and -propyl-catechol. By GEORGE BARGER 2081

CCVII.—The Synthesis of Thionaphthen Derivatives from Styrenes and Thionyl Chloride. By GEORGE BARGER and ARTHUR JAMES EWINS 2086

CCVIII.—Organic Derivatives of Silicon. Part VIII. The Resolution of *dl*-Sulphobenzylethyl*iso*butylsilicyl Oxide and the Properties of the Optically Active Acids. By BERNARD DUNSTAN WILKINSON LUFF (1851 Exhibition Scholar) and FREDERIC STANLEY KIPPING 2090

CCIX.—Some Molecular Compounds of Styphnic and Picric Acids. By CHARLES STANLEY GIBSON 2098

CCX.—The Formation of Some Carbides. By JOHN NORMAN PRING 2101

CCXI.—The Relation between Absorption Spectra and Chemical Constitution. Part XII. Some Amino-aldehydes and -ketones of the Aromatic Series. By EDWARD CHARLES CYRIL BALY and EFFIE GWENDOLINE MARSDEN 2108

CCXII.—The Affinity of Certain Alkaloids for Hydrochloric Acid. By VICTOR HERBERT VELEY 2114

CCXIII.—The Affinity Constants of Bases as Determined by the Aid of Methyl-Orange. By VICTOR HERBERT VELEY . 2122

CCXIV.—Organic Derivatives of Arsenic. Part I. Dicamphorylarsinic Acid. By GILBERT T. MORGAN and FRANCES M. G. MICKLETHWAIT 2144

CCXV.—Study of the Constitution and Properties of the Rhodanides of Inorganic Radicles. Part I. By AUGUSTUS EDWARD DIXON and JOHN TAYLOR 2148

CCXVI.—Ester Catalysis and a Modification of the Theory of Acids. By EDWARD FITZGERALD and ARTHUR LAPWORTH . 2163

CCXVII.—Tellurium Dicyanide. By HERBERT EDWIN COCKSEDGE 2175

CCXVIII.—Boron Thiocyanate. By HERBERT EDWIN COCKSEDGE 2177

CCXIX.—The Viscosity of Fuming Sulphuric Acid. By ALBERT ERNEST DUNSTAN and ROBERT WILLIAM WILSON . 2179

CCXX.—The Densities of Krypton and Xenon. By RICHARD B. MOORE, B.Sc. 2181

CCXXI.—An Examination of the Conception of Hydrogen Ions in Catalysis, Salt Formation, and Electrolytic Conduction. By ARTHUR LAPWORTH 2187

CCXXII.—The Oxidation of Phosphorous Acid by Iodine. By BERTRAM DILLON STEELE 2203

OBITUARY 2214

JOURNAL

OF

THE CHEMICAL SOCIETY.

TRANSACTIONS.

I.—*The Relation Between Unsaturation and Optical Activity. Part I. The Menthyl and Bornyl Esters of β-Phenylpropionic, Cinnamic, and Phenylpropiolic Acids.*

By Thomas Percy Hilditch.

The connexion between the degree of unsaturation and the rotatory power of an optically active compound was studied in detail by Walden (*Zeitsch. physikal. Chem.*, 1896, **20**, 569), who noticed that Guye's hypothesis that the rotation of a compound depends on the masses of the groups surrounding the asymmetric carbon atom does not account for the great alteration in activity which, as a general rule, accompanies ring-formation. He was consequently led to investigate the effect of changes in constitution on rotatory power, and commenced by taking the case in which change of constitution was associated with a minimum alteration of molecular weight, that is, the change from a saturated to an ethylenic, and from the latter to an acetylenic linking. From a comparison of the rotatory powers of a series of *l*-amyl esters of six pairs of corresponding saturated and ethylenic mono-, di-, and tri-basic aliphatic acids, it was found that the unsaturated ester possessed in all cases a slightly greater rotation than the saturated compound, although in no case was the rotation large. Again, with the *l*-amyl esters of β-phenylpropionic acid, cinnamic acid, and phenylpropiolic acid, the following figures were obtained:

		$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
β-Phenylpropionic ester ...	$C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2{\cdot}C_5H_{11}$	+2·26°	+4·98°
Cinnamic ester	$C_6H_5{\cdot}CH{:}CH{\cdot}CO_2{\cdot}C_5H_{11}$	7·51	16·36
Phenylpropiolic ester	$C_6H_5{\cdot}C{\vdots}C{\cdot}CO_2{\cdot}C_5H_{11}$	5·58	12·05

The results for diamyl succinate, fumarate, and acetylenedicarboxylate were of a similar nature, although actual figures for the last ester were not given, as it was not obtained quite pure.

From the above facts, Walden deduced that when a single bond is converted into a double one by the loss of two hydrogen atoms, the molecular rotatory power of the substance is increased; but that a further change to a triple bond diminishes it, although it does not cause it to fall so low as that of the fully saturated compound. Lately, however (*Zeitsch. physikal. Chem.*, 1906, **55**, 1), he has stated that the *l*-amyl alcohol used in the preparation of the esters was not optically pure, but that this does not affect the value of his results for purposes of comparison. It appeared desirable, in view of this and also of the fact that certain isolated observations have been made which do not bear out Walden's rule, to obtain more comprehensive data on the subject, and the author has therefore studied the menthyl and bornyl esters of the same series of acids. In the present paper, the results obtained with the menthyl and bornyl esters of β-phenylpropionic, cinnamic, and phenylpropiolic acids are described, and it may be said that these do not give unqualified confirmation to Walden's generalisation.

Before giving a detailed account of these experiments, it will be useful to refer to examples of the change of rotatory power accompanying this change of constitution, which have been observed since Walden published his results.

Tschugaeff (*Ber.*, 1898, **31**, 360, 1775) has measured the rotations of a large series of menthyl and bornyl esters of fatty acids in order to determine whether optical activity is influenced more by the mass or the constitution of the optically active molecule; from his results, together with similar data on homologous series of various optically active esters, ethers, acylamines, &c., compiled by Guye and Chavanne (*Compt. rend.*, 1895, **120**, 452), Frankland and MacGregor (Trans., 1893, **63**, 511, 1410), Frankland (Trans., 1899, **75**, 347), and others, he concluded that the molecular rotation in an homologous series increases to an approximately constant value on ascending the series. He found that this rule does not hold if an aromatic group is present in the molecule, unless the aromatic group is situated at some distance from the asymmetric carbon atom. The following numbers show this clearly:

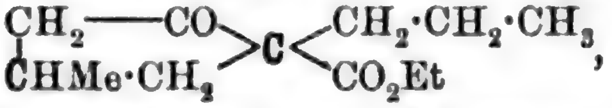
		$[M]_D$.
Menthyl benzoate	$C_6H_5\cdot CO_2\cdot C_{10}H_{19}$	−236·3°
,, phenylacetate	$C_6H_5\cdot CH_2\cdot CO_2\cdot C_{10}H_{19}$	190·7
,, β-phenylpropionate .	$C_6H_5\cdot CH_2\cdot CH_2\cdot CO_2\cdot C_{10}H_{19}$	161·9

The average value of the molecular rotation for a menthyl fatty acid ester is −157·8°. Hence the phenyl group, when in close proximity to the optically active part of the molecule, exercises a disturbing influence on the latter, but the variation depends entirely on the relative position of the aromatic group, and almost disappears if the group in question is not in the immediate neighbourhood of the asymmetric carbon atom.

The same author (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 606) prepared menthyl β-phenylpropionate and cinnamate, and found a large increase of rotation for the latter, thus:

	$[\alpha]_D$.
Menthyl β-phenylpropionate	−56·21°
,, cinnamate	−86·65

The latter result, however, is not confirmed by the present work, as will be shown later.

Haller and Desfontaines (*Compt. rend.*, 1903, **136**, 1613) have mentioned that, whilst ethyl 4-methyl-1-*n*-propyl-2-*cyclo*pentanone-2-carboxylate,  $\begin{matrix}CH_2\text{——}CO\\ CHMe\cdot CH_2\end{matrix}>C<\begin{matrix}CH_2\cdot CH_2\cdot CH_3\\ CO_2Et\end{matrix}$, has a specific rotation $[\alpha]_D$ +51·8°, the corresponding ethyl 4-methyl-1-allyl-2-*cyclo*pentanone-2-carboxylate possesses a higher value, namely, $[\alpha]_D$ +62·54°, whilst Klages and Sautter (*Ber.*, 1904, **37**, 649) found that the specific rotation of α-phenyl-γ-methylpentane, $CH_2Ph\cdot CH_2\cdot CHMeEt$, was +17·2°, whereas that of α-phenyl-γ-methyl-Δ^{α}-pentene was +43°.

Finally, Minguin (*Compt. rend.*, 1905, **140**, 946), in discussing the influence of the ethylenic linking in an active molecule, has decided that an increase in unsaturation is accompanied by an increase in optical activity from a consideration of the following figures:

	α.		α.
Amyl succinate	+ 9° 0′	Bornyl succinate	−1°22′
,, fumarate	+15 40	,, fumarate	−1 42
,, butyrate........	+ 2 46	,, butyrate	−4 30
,, crotonate	+ 3 30	,, crotonate	−4 44

He explains the small difference in the rotation of the corresponding bornyl esters as being due to the fact that these were measured in solution, whereas the amyl compounds were measured in the liquid state. The rotations themselves are certainly very small, but the minute increase surely cannot be safely ascribed to the influence of the solvent, for it is an almost invariable rule that solution in an inactive non-associating solvent has little effect on the rotatory power. Two samples of this may be given from the present work:

Rotation of	In fused state. $[\alpha]_D$.	5% solution in chloroform. $[\alpha]_D$.
l-Menthol.....................	−49·88° (Biltz).	−48·40°
l-Menthyl β-phenylpropionate...	−56·21 (Tschugaeff).	−57·90

In the first case, the rotatory power is slightly decreased in solution; in the second, it is increased, but in both instances the change does not materially affect the magnitude of the optical activity.

EXPERIMENTAL.

It was decided to use menthyl and bornyl esters for the purposes of this investigation, since derivatives of these alcohols possess, in general, a fairly large rotation, and, in addition, are easily obtained in a pure state. The esters were prepared by either of two methods:

(1) The acid was treated with excess of thionyl chloride and heated to 100°; the resulting acid chloride, which was practically pure (and was not contaminated by inorganic impurities as would have been the case if phosphorus pentachloride had been used), was then mixed with a slight excess of the alcohol and heated at 120° until the evolution of hydrogen chloride ceased.

(2) The alcohol and acid, the former usually in slight excess, were heated in a stream of hydrogen chloride at 130—140° for some hours.

After elimination of traces of acid by dilute alkali, the esters were purified by distillation under reduced pressure. The high temperature of distillation appeared to have little effect on the rotation, and it was found that practically no decomposition of the compounds occurred under these conditions, except in the case of the esters of phenylpropiolic acid. The purity of each of the compounds was checked by analysis and by measurement of the rotation of the menthol recovered from the esters by hydrolysis.

The specific gravities were measured in an Ostwald-Sprengel pyknometer maintained at constant temperature (17°), or, in the case of the solid esters, filled as near the melting point as possible; the values obtained were referred to water at 4°. The refractive indices of the esters in the liquid or superfused state were also observed by means of an Abbé refractometer, and it may be mentioned as indicative of the degree of purity of the specimens used, that in the case of those solid at the ordinary temperature it was exceedingly difficult to maintain them in the superfused condition more than a degree or two below their melting points.

As several experimental difficulties stood in the way of determining the specific rotations of the esters themselves, it was decided to examine them in solution. In order to be sure that the solvent exerted no disturbing effect, the rotations were measured in both of two chemically dissimilar solvents, chloroform and acetone, and in both cases the measurements were carried out at three different concentrations of the dissolved ester. The polariscope tube was surrounded by a metal jacket through which a current of cold water was passed at a regular rate; the temperature of each observation was noted, and varied between the extreme values of 20° and 22° for the whole series of experiments; a 2-dcm. tube was used throughout. The numbers given in the following tables show that, in general, the rotatory power varies very slightly with the solvent, and in a corresponding manner for all the substances on dilution, so that comparisons between the optical rotatory powers of the various esters may be legitimately deduced from them, since it is obvious from the regular variation of the rotation with dilution that no association of the molecules of any of the esters occurs.

Menthyl β-Phenylpropionate, $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2{\cdot}C_{10}H_{19}$.

Eight grams of β-phenylpropionic acid were heated on the water-bath with excess of thionyl chloride until no more hydrogen chloride was evolved, and the mixture was then treated with a slight excess of menthol and heated to 120° for some time. The product was shaken with dilute sodium carbonate solution, extracted with ether, dried, and, after removal of the ether, fractionated in a vacuum. The fraction boiling from 208° to 213° was collected, and it solidified on cooling in a freezing mixture.

The rotation of this ester in the superfused state and also its density have been determined by Tschugaeff (*loc. cit.*), who, however, gives no further description of its properties. It is a waxy solid, crystallising in short prisms, which melt at 28° to a colourless liquid boiling at 210—212° (25 mm.). Its specific gravity at its fusion point is $d\ 28^\circ/4^\circ = 0{\cdot}9836$ (0·9851 : Tschugaeff), and its refractive index $n_D^{17^\circ} = 1{\cdot}5004$:

0·1376 gave 0·3975 CO_2 and 0·1252 H_2O. C = 78·77 ; H = 10·11.

$C_{19}H_{28}O_2$ requires C = 79·17 ; H = 9·72 per cent.

The following table gives the measurements obtained for the rotatory power of this substance :

Percentage concentration.	Solution in chloroform.				Solution in acetone.			
	Temp.	a.	$[a]_D$.	$[M]_D$.	Temp.	a.	$[a]_D$.	$[M]_D$.
10	20°	−11·91	−59·55	−171·5	21°	−11·29	−56·45	−162·6
5	20	5·93	59·30	170·8	22	5·79	57·90	166·8
2½	20	3·04	60·80	175·1	21	3·00	60·00	172·8

Menthyl Cinnamate, $C_6H_5\cdot CH\colon CH\cdot CO_2\cdot C_{10}H_{19}$.

This compound is mentioned by Cohen and Whiteley (Trans., 1901, **79**, 1308), who obtained it as a pale yellow, non-crystallisable oil from equivalent quantities of cinnamyl chloride and menthol, but did not investigate it further. Tschugaeff (*loc. cit.*) found a value $[\alpha]_D$ −86·65° for the specific rotation, which is widely different from those determined by the author. The specimen used was obtained from cinnamic acid by the same method as that by which menthyl β-phenylpropionate was prepared. After two fractionations in a vacuum, it was an almost colourless, viscous oil, boiling at 230—233° (27 mm.); it did not solidify at −15°, but at that temperature became so viscous that the vessel containing it could be inverted without causing the contents to flow perceptibly; d 17°/4° = 1·0079 (1·0066 : Tschugaeff); specific refractive index $n_D^{17°}$ = 1·5433 :

0·1856 gave 0·5440 CO_2 and 0·1538 H_2O. C = 79·89 ; H = 9·21.

$C_{19}H_{26}O_2$ requires C = 79·72 ; H = 9·09 per cent.

The following rotations were observed with solutions of this ester :

Percentage concentration.	Solution in chloroform.				Solution in acetone.			
	Temp.	α.	$[\alpha]_D$.	$[M]_D$.	Temp.	α.	$[\alpha]_D$.	$[M]_D$.
10	20°	−12·00	−60·00	−171·6	−21	−12·89	−64·45	−184·3
5	20	5·99	59·90	171·3	21	6·29	62·90	179·9
2½	21	3·04	60·80	173·9	21	3·18	63·60	181·9

Menthyl Phenylpropiolate, $C_6H_5\cdot C\colon C\cdot CO_2\cdot C_{10}H_{19}$.

This was prepared by heating 5 grams of phenylpropiolic acid with a slight excess of menthol to 140° in an oil-bath for about four hours, a stream of dry hydrogen chloride being passed through the mixture continuously. By this means, after washing the product with dilute sodium carbonate solution, extracting with ether, drying, and fractionating, a yield of 7½ grams of ester, boiling at 232—240° (30 mm.), was obtained.

This was refractionated and the portion boiling at 235—238° (30 mm.) collected. This solidified, on cooling, to a mass of slightly yellow crystals, melting at 33°. The specific gravity at the melting point of the compound was d 33°/4° = 1·0595, and the specific refractive index of the supercooled liquid was $n_D^{17°}$ = 1·5239 :

0·1123 gave 0·3291 CO_2 and 0·0897 H_2O. C = 79·92 ; H = 8·88.

$C_{19}H_{24}O_2$ requires C = 80·28 ; H = 8·45 per cent.

The following measurements of the rotatory power were carried out :

Percentage concentration.	Solution in chloroform.				Solution in acetone.			
	Temp.	α.	[α]D.	[M]D.	Temp.	α.	[α]D.	[M]D.
10	21°	−11·73	−58·65	−166·7	21°	−11·11	−55·55	−157·6
5	20	5·70	57·00	161·9	21	5·26	52·60	149·4
2½	21	3·01	60·20	171·0	20	2·62	52·40	148·8

Bornyl β-Phenylpropionate, $C_6H_5\cdot CH_2\cdot CH_2\cdot CO_2\cdot C_{10}H_{17}$.

This ester was prepared by the thionyl chloride method from 7 grams of the acid and an equivalent amount of borneol. After two fractionations in a vacuum, a yellow oil boiling at 205—207° (20 mm.) resulted, which had a specific gravity d 17°/4° = 1·0350 and a specific refractive index $n_D^{17°} = 1·5142$. On analysis:

0·0820 gave 0·2388 CO_2 and 0·0668 H_2O. C = 79·43; H = 9·05.
$C_{19}H_{26}O_2$ requires C = 79·72; H = 9·09 per cent.

The results obtained for the optical rotatory power were as follows:

Percentage concentration.	Solution in chloroform.				Solution in acetone.			
	Temp.	α.	[α]D.	[M]D.	Temp.	α.	[α]D.	[M]D.
10	20°	+6·05	+30·25	+86·5	20°	+5·80	+29·00	+82·9
5	20	2·95	29·50	84·4	22	2·80	28·00	80·1
2½	20	1·46	29·20	83·5	22	1·46	29·20	83·5

Bornyl Cinnamate, $C_6H_5\cdot CH\cdot CH\cdot CO_2\cdot C_{10}H_{17}$.

This was obtained by the hydrochloric acid method, the oil-bath being maintained at about 130° for five hours. On purification and fractionation, a pale yellow oil was collected, which distilled at 226—230° (27 mm.) and did not solidify on cooling. Its specific gravity was d 17°/4° = 1·0571, and its refractive index $n_D^{17°} = 1·5525$:

0·1374 gave 0·4063 CO_2 and 0·1075 H_2O. C = 80·63; H = 8·70.
$C_{19}H_{24}O_2$ requires C = 80·28; H = 8·45 per cent.

The following polarimetric observations were made:

Percentage concentration.	Solution in chloroform.				Solution in acetone.			
	Temp.	α.	[α]D.	[M]D.	Temp.	α.	[α]D.	[M]D.
10	21°	+5·81	+29·05	+82·5	20°	+5·82	+29·10	+82·6
5	22	2·80	28·00	79·5	21	2·68	26·80	76·1
2½	21	1·42	28·40	80·7	22	1·38	27·60	78·4

Bornyl Phenylpropiolate, $C_6H_5\cdot C⋮C\cdot CO_2\cdot C_{10}H_{17}$.

This compound was prepared by the hydrochloric acid method from 5 grams of the acid and a slight excess of borneol. In this way, nearly 4 grams of ester were finally obtained as a pale yellow, crystalline mass, melting at 45°, and boiling at 228—230° (21 mm.). The specific gravity of the crystals at the melting point was $d\ 45°/4° = 1·0884$, and the refractive index of the supercooled liquid was $n_D^{17} = 1·5500$:

0·1002 gave 0·2951 CO_2 and 0·0742 H_2O. C = 80·32 ; H = 8·23.

$C_{19}H_{22}O_2$ requires C = 80·85 ; H = 7·80 per cent.

The optical rotatory powers measured were :

Percentage concentration.	Solution in chloroform.				Solution in acetone.			
	Temp.	α.	$[\alpha]_D$.	$[M]_D$.	Temp.	α.	$[\alpha]_D$.	$[M]_D$.
10	21°	+6·21	+31·05	+87·6	20°	+6·34	+31·70	+89·4
5	22	3·13	31·30	88·3	20	3·10	31·00	87·4
2½	22	1·57	31·40	88·6	22	1·51	30·20	85·2

The above observations show that there is no conspicuous alteration in optical activity in either series of esters, but at the same time certain small, but well-defined, variations are to be noted, and these are apparently closely connected with the degree of unsaturation of the acid present. In order to present these comparative differences more clearly, two tables are given showing the molecular rotations of each series of esters at corresponding concentrations (the specific rotations, it will be noticed, are related similarly, owing to the small change of molecular weight of the esters).

I. *Menthyl Esters.*

Acid.	Solution in chloroform.			Solution in acetone.		
	10 %.	5 %.	2½ %.	10 %.	5 %.	2½ %.
β-Phenylpropionic ...	−171·5	−170·8	−175·1	−162·6	−166·8	−172·8
Cinnamic	171·6	171·3	173·9	184·3	179·9	181·9
Phenylpropiolic.........	166·7	161·9	171·0	157·6	149·4	148·8

II. *Bornyl Esters.*

Acid.	Solution in chloroform.			Solution in acetone.		
	10 %.	5 %.	2½ %.	10 %.	5 %.	2½ %.
β-Phenylpropionic ...	+86·5	+84·4	+83·5	+82·9	+80·1	+83·5
Cinnamic	82·5	79·5	80·7	82·6	76·1	78·4
Phenylpropiolic.........	87·6	88·3	88·6	89·4	87·4	85·2

It will now at once be perceived, first, that with only one exception, the change of rotation is in the same direction for corresponding concentrations of the esters in either solvent ; and, further, that in the case of the menthyl esters, the ester containing a "doubly-linked" pair of carbon atoms has a slightly (numerically) increased rotation compared with the saturated ester, whilst the ester of the acetylenic acid possesses less rotatory power than even the saturated ester : whereas the converse holds for the corresponding bornyl esters, a change from a saturated to an ethylenic linking being now accompanied by a (numerical) decrease of rotatory power, whilst, on the other hand, a further increase of unsaturation produces an ester the optical activity of which is numerically greater than that of the saturated ester. The only exception to this rule in the observations quoted above is the rotation of a 2½ per cent. solution of menthyl cinnamate in chloroform; this may safely be attributed to errors of experiment, as at this dilution the angle of rotation observed is small enough to give a large discrepancy in the molecular rotation for a comparatively small error of observation. The relative differences in optical activity appear to be more accentuated in the case of solutions in acetone of the menthyl esters than in any other instance; the precise reason for this is not obvious.

The above experiments furnish further data for discussion of the following two points:

(1) The steady change in optical activity which is found to accompany changes from saturated to ethylenic, and from the latter to acetylenic, linkings in a compound.

(2) The small relative change of the rotation of the various esters.

The results obtained evidently do not agree entirely with Walden's statement; it will therefore be necessary to examine them in further detail. In the first place, Walden prepared his esters from *l*-amyl alcohol, and, in accordance with the well-known rule, invariably obtained dextrorotatory esters; thus the influence of the acid is to change the sign of the rotation, or, in other words, to exert a preponderatingly positive influence. In the case of the menthyl esters described above, the specific rotations varied between the extremes of α_D^{20} $-52{\cdot}40°$ for a 2½ per cent. solution of menthyl phenylpropiolate in acetone and $[\alpha]_D^{21}$ $-64{\cdot}45°$ for a 10 per cent. solution of menthyl cinnamate in acetone. A sample of the menthol used to prepare the esters was examined in the polariscope with the following result. A 5 per cent. solution in chloroform at 20° in a 2-dcm. tube gave a rotation, $\alpha - 4{\cdot}84°$, whence $[\alpha]_D^{20}$ $-48{\cdot}40°$, and $[M]_D^{20}$ $-75{\cdot}50°$. Again, some of the menthyl cinnamate on hydrolysis with alcoholic potash, after dilution and extraction with ether, gave a specimen of menthol which after recrystallisation melted at 41·5°, and a 5 per cent. solution of this in chloroform in a 1-dcm. tube at 20° gave $\alpha - 2{\cdot}40°$, $[\alpha]_D^{20}$ $-48{\cdot}00°$, and $[M]_D^{20}$ $-74{\cdot}88°$. This affords proof of the optical purity of the esters, and also shows that the rotation of the esters was always greater than that of menthol itself.

With the bornyl compounds, the specific rotations varied between that of a 5 per cent. solution in acetone of bornyl cinnamate, $[\alpha]_D^{21}$ $+26{\cdot}80°$, and that of a 10 per cent. solution in acetone of bornyl phenylpropiolate, $[\alpha]_D^{20}$ $+31{\cdot}70$, whereas the specific rotation of the borneol used was $+35{\cdot}9°$ before esterification and $+34{\cdot}8°$ after recovery from one of the esters.

Hence, in one case, the introduction of the acidic radicle causes an increase, and, in the other, a decrease of rotatory power. Although the direction of the change is thus shown not to be uniform in all cases, it is quite possible that the change of rotation on esterification depends chiefly on the nature of the optically active alcohol; indeed, a difference of behaviour between alcohols of widely varying structure, configuration, and optical activity is only to be expected; this view is borne out by Guye's work on the influence of mass on rotatory power. But, at the same time, one would expect the change of optical activity occasioned by unsaturation in any asymmetric compound to be dependent solely on the change from single to double, or double to triple bonds, and, granting that this is the only factor influencing the alteration in rotation, it follows that the optical effects produced should lie in a corresponding direction for each stage of unsaturation with any alcohol. If this is the case, it is likely that the change in rotation will depend in some way on the influence which any acidic group exerts on the molecule.

To illustrate this, the following tables have been drawn up, in which the numbers given represent the difference between the specific rotations observed above and the specific rotation of menthol ($[\alpha]_D - 48·4°$) and borneol ($[\alpha]_D + 37·0°$):

I. *Menthyl Esters.*

	Solution in chloroform.			Solution in acetone.		
Acid.	10 %.	5 %.	2½ %.	10 %.	5 %.	2½ %.
β-Phenylpropionic.........	11·1	10·9	12·4	8·0	9·5	11·6
Cinnamic	11·6	11·5	12·4	16·0	14·5	15·2
Phenylpropiolic	10·2	8·6	11·8	7·1	4·2	4·0

II. *Bornyl Esters.*

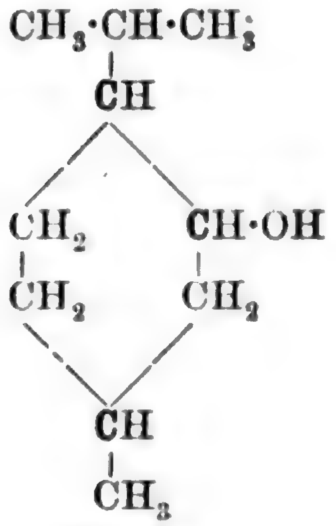
	Solution in chloroform.			Solution in acetone.		
Acid.	10 %.	5 %.	2½ %.	10 %.	5 %.	2½ %.
β-Phenylpropionic.........	6·7	7·5	7·8	8·0	9·0	7·8
Cinnamic	7·9	9·0	8·6	7·9	10·2	9·4
Phenylpropiolic	5·9	5·7	5·6	5·3	6·0	6·8

In accordance with the numbers obtained, it will be assumed for the moment that the presence of an ethylenic linking causes a further increase in the effect produced by the saturated acidic radicle, whilst an acetylenic linking decreases this effect. It is shown above that the effect of the entry of a saturated acidic group into the lævo-menthol molecule is to increase the negative specific rotation; a change from such an ester to the corresponding ethylenic compound produces an increase in the negative specific rotation, and a further change to the acetylenic ester causes the specific rotation to fall to less than that of the saturated substance. The case is slightly different for the bornyl derivatives, for here it will be observed that the acidic radicle exerts a diminishing influence on the specific rotation; hence, proceeding on the assumption made above, an alteration from a single to a double bond should increase this negative influence, whilst, conversely, the change from a single to a triple linking should lessen the negative influence of the acidic radicle and so increase the positive rotation: this is exactly what has been observed to take place.

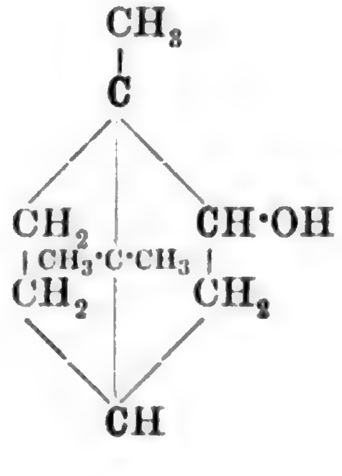
Bearing in mind, then, that in the case of esters a change of rotation is to be considered with reference to the direction of the change of rotation which occurs on esterification of the active alcohol by any inactive acid whatever, the results obtained indicate that the presence of an ethylenic bond in a compound increases the optical activity, whereas that of an acetylenic bond causes the rotation to be less than that of the saturated compound.

The question now arises, how far does this conception agree with other work which has been done on the subject? So far as the effect of the ethylenic linking is concerned, the results now put forward serve to corroborate all the observations quoted in an earlier part of this paper; in the case of compounds such as those prepared by Haller and Desfontaines, and by Klages and Sautter (*loc. cit.*), there is no question of the change which the group containing the unsaturated part of the molecule exerts on the rotation of the molecule as a whole, and therefore a simple increase of rotation takes place. Minguin's and Walden's results for esters of *l*-amyl alcohol also show that an increase of optical activity accompanies the change from a single to a double bond, and Hartwall (*Diss.*, Helsingfors, 1904) has obtained similar results with active hydroaromatic esters of aliphatic acids, but if the above assumption is extended to Walden's results for the active amyl esters of phenylpropiolic and acetylenedicarboxylic acids (the actual numbers for the latter substance are not given), it is obvious that a decrease in rotation should be found, whereas this author states that the numerical value of the optical activity lies between those of the corresponding saturated and ethylenic compounds. Since Walden has himself admitted that the alcohol used was not optically pure, it would appear probable that these results are inaccurate, and that the change to a triple bond causes decrease in optical rotatory power. It may here be mentioned that Stewart (Trans., 1907, **91**, 199), in dealing with the relation between absorption spectra and optical rotatory power, observed that neither the order of the persistence of the absorption bonds nor of the frequencies at their heads appeared to be connected with the order in which the rotations (according to Walden) stood; but it will be noted that the order of both of these coincides with that now determined for the effect of unsaturation, so that the order of the variation of rotation with unsaturation does not present any obstacle to the deduction of relations between the two series of phenomena.

It would seem that some explanation is desirable of the notably small, although regular, changes experienced in the rotations of these esters. Many investigations have served to give prominence to the fact that optical activity is not, as Guye at first supposed, simply a function of the masses surrounding the asymmetric carbon atom, but depends also on the constitution of the molecule; it appears to the author that the present research serves especially well to display the influence both of the mass and of the constitution of the molecule; for, whilst the effect of unsaturation is shown to produce perfectly definite changes in the rotatory power, the mass of the ester is in all cases so great that these changes are quite small in comparison with the average specific rotation. Now, if the structural formulæ adopted for menthol and borneol are considered, it at once becomes evident that the three asymmetric carbon atoms are similarly situated in each molecule, thus:



Menthol.



Borneol.

it is therefore natural, according to Guye's view, that the effect of a small change in the weight of the molecule should be approximately the same in each case, and also that in neither case should a very marked change of optical activity occur. Further, it has been observed (Guye and Babel, *Arch. Sci. phys. nat.*, 1899, [iii], **7**, 114; Guye, Trans., 1901, **79**, 476) that substitution in an optically active compound effected at a point sufficiently far removed from the asymmetric carbon atom scarcely modifies the rotatory power. This fact may be illustrated by McCrae's work on ethyl octyl tartrate (Trans., 1901, **79**, 1106), in which the following results for derivatives of this substance were obtained:

	$[M]_D^{20^\circ}$		$[M]_D^{20^\circ}$.
Diethyl tartrate	+15·78°	Ethyl octyl tartrate	+22·55°
,, diacetyltartrate	+9·9	,, ,, diacetyltartrate ...	+15·8
,, dibenzoyltartrate......	−247·1	,, ,, dibenzoyltartrate.	−245·8

It will be noted that the difference between the values for corresponding derivatives of ethyl octyl and diethyl tartrate (which are also given in the table) is relatively small in each case. Equally instructive is the case of the menthyl esters of benzoic, phenylacetic, and β-phenylpropionic acids, which, as has been mentioned (p. 2), has been investigated by Tschugaeff.

Again, Haller and Desfontaines (*loc. cit.*) observed a comparatively small increase of activity in corresponding saturated and unsaturated derivatives of *cyclo*pentanone containing two asymmetric carbon atoms, of which only one was situated close to that part of the molecule where change of constitution was effected. These instances show that with many compounds of fairly high molecular weight a slight change in constitution is not usually accompanied by any great alteration in optical activity.

Rupe (*Annalen*, 1903, **327**, 157) has made an extensive study of a case which, however, is even more closely related to the nature of the present work, namely, the effect of the position of the double bond on the optical activity of a large series of menthyl esters. His most interesting results are collected in the following tables:

Menthyl esters of	$[\alpha]_D$.	$[M]_D$.
Crotonic acid	−90·67°	−203·1°
$\Delta^{\alpha\beta}$-Pentenoic acid	74·41	177·1
$\Delta^{\beta\gamma}$-Pentenoic ,, ...	72·51	172·5
$\Delta^{\gamma\delta}$-Pentenoic ,, ...	67·32	160·2
$\Delta^{\alpha\beta}$-Hexenoic ,, ...	68·38	172·4
$\Delta^{\beta\gamma}$-Hexenoic ,, ...	65·11	164·1
$\Delta^{\gamma\delta}$-Hexenoic ,, ...	60·93	153·5
$\Delta^{\delta\epsilon}$-Hexenoic ,, ...	61·25	154·4
$\Delta^{\alpha\beta}$-Heptenoic ,, ...	66·03	175·5

Thus in the case of aliphatic unsaturated acids, the double bond exerts less and less influence the further it is away from the asymmetric carbon atom. He shows, moreover, that a similar state of affairs prevails with the reduced benzoic acids, thus:

Menthyl esters of	$[\alpha]_D$.
Benzoic acid	−83·53°
Δ^1-*cyclo*Hexenecarboxylic acid	74·64
Δ^2-*cyclo*Hexenecarboxylic acid	59·44
*cyclo*Hexanecarboxylic acid	59·11

It will be especially noted in this connexion that the Δ^2-*cyclo*hexenecarboxylic acid has much less effect than the Δ^1-acid, the double linking being further removed from the asymmetrical part of the molecule.

These instances, then, show clearly that a large alteration of rotation is not to be looked for in the case of esters, such as those of menthol and borneol, containing no less than three asymmetric carbon atoms, two of which at least are relatively distantly situated with respect to the point where change in constitution takes place, and it may be held that the behaviour of these esters is quite in accordance with what might have been expected from due consideration of previous observations.

Attention may be drawn to the fact that other physical properties of the esters appear to be influenced in a regular manner by increase of unsaturation; thus the boiling points and specific gravities appear to increase with increasing unsaturation, whilst the refractive index increases for a change from single to double, but decreases to an intermediate value for the further change to a triple, bond. The following table illustrates these properties, together with the values for a typical corresponding set of polarimetric measurements:

				10 per cent. solution.			
				Chloroform.		Acetone.	
Ester.	B. p.	Sp. gr.	Refractive index.	$[\alpha]_D$.	$[M]_D$.	$[\alpha]_D$.	$[M]_D$.
Menthyl β-phenylpropionate	210—212° (25 mm.)	0·9836	1·5004	−59·55°	−171·5°	−56·45°	−162·6°
Menthyl cinnamate..................	230—233° (27 mm.)	1·0079	1·5433	−60·00	−171·6	−64·45	−184·3
Menthyl phenylpropiolate	235—238° (30 mm.)	1·0595	1·5239	−58·65	−166·7	−55·55	−157·6
Bornyl β-phenylpropionate	205—207° (20 mm.)	1·0350	1·5142	+30·25	+86·5	+29·00	+82·9
Bornyl cinnamate.	226—230° (27 mm.)	1·0571	1·5525	+29·05	+82·5	+29·10	+82·6
,, phenylpropiolate	228—230° (21 mm.)	1·0884	1·5500	+31·05	+87·6	+31·70	+89·4

The author is at present engaged in an investigation of the menthyl and bornyl esters of succinic, fumaric, and acetylenedicarboxylic acids, and by comparing the optical rotatory powers of these under similar conditions it is hoped to obtain still further data on which to base some generalisation of the relation between unsaturation and optical activity. In the meantime, the following summary may be given of the conclusions so far arrived at:

(1) The effect of change from a saturated to a corresponding unsaturated compound produces a relatively small change in the case of the rotation of esters of menthol and borneol.

(2) These alterations are nevertheless perfectly definite, and exhibit quite regular fluctuations depending on the change of constitution.

(3) The conversion of a saturated to an ethylenic linking is

accompanied by an increase in rotatory power, whilst the change from a saturated to an acetylenic bond is apparently connected with a decrease in rotatory power.

(4) In the case of esters, the change in rotation must be measured with respect to the influence which any acidic group exerts on the molecule, or, in other words, with reference to the difference between the specific rotation of the ester and that of the active alcohol from which it was formed.

(5) Walden's results are thus confirmed so far as the change to an ethylenic linking is concerned, but there is a discrepancy as regards the influence of the triple bond on the optical activity; he does not, however, appear to have recognised the necessity of observing the last-mentioned distinction with regard to esters.

In conclusion, the author desires to thank Prof. Collie and Dr. Smiles for the interest they have shown in this research, and to acknowledge his indebtedness to Dr. A. W. Stewart for much valuable assistance in the course of the work.

THE ORGANIC CHEMISTRY LABORATORY,
UNIVERSITY COLLEGE,
LONDON.

II.—*Note on the Iodates and Periodates of the Alkali Metals and the Ammonium Radicle.*

By THOMAS VIPOND BARKER, B.A., B.Sc.(Oxon.).

THE present communication deals with the chemical part of an investigation of certain iodates and periodates which were chiefly prepared for a crystallographic examination; the results of the latter will appear shortly in the *Zeitschrift für Krystallographie.*

Of the analyses, the halogen estimations were effected by the Carius method, which the author had previously found to answer well for the perchlorates; the heating was carried out in two operations, each lasting four hours, the first to 150° and the second to 250°. The metal was estimated by the usual sulphate method.

The specific gravity determinations were made in capped specific gravity bottles with carbon tetrachloride as displacing liquid; the solubility determinations were carried out with 20 c.c. of the saturated solutions.

Rubidium Iodate, $RbIO_3$.—This salt, as well as the corresponding cæsium compound, was first prepared by Wheeler (*Amer. J. Sci.*, 1902, [iii], **44**, 123) by adding iodic anhydride to solutions of the carbonates. A good yield is obtained by passing chlorine into a hot concentrated solution of a mixture of rubidium iodide and hydroxide, whereby the sparingly soluble iodate is precipitated:

Specific gravity at 14°/4° = 4·559. Mol. vol. = 57·14.

Solubility: 100 parts of water dissolve 2·1 parts at 23° (Wheeler).

Caesium Iodate, $CsIO_3$.—This salt was prepared in the same way as the rubidium compound:

Specific gravity at 16°/4° = 4·831. Mol. vol. = 63·68.

Solubility: 100 parts of water dissolve 2·6 parts at 24° (Wheeler).

The iodates of potassium, rubidium, and cæsium form an isomorphous group, crystallising in what appear to be cubes, but which are really made up of four monoclinic sub-individuals, interpenetratingly twinned.

Potassium periodate, KIO_4, is readily prepared by oxidising the iodate; a suitable method is to pass chlorine into a hot, strongly alkaline solution of the iodate (Rammelsberg, *Ann. Phys. Chem.*, 1868, [ii], **134**, 368); the very sparingly soluble periodate separates in tetragonal bipyramids *:

0·3080 gave 0·3106 AgI. I = 54·5.

KIO_4 requires I = 55·1 per cent.

Specific gravity at 15°/4° = 3·618. Mol. vol. = 63·60.

Solubility: 100 parts of water dissolve 0·66 part at 13°, and the specific gravity of the saturated solution at 13°/4° is 1·0051.

Rubidium periodate, $RbIO_4$, has not previously been obtained. It was prepared by the method mentioned above for the potassium compound. The precipitated crystals were washed and recrystallised twice:

0·3090 gave 0·2664 AgI. I = 46·6.
0·4045 „ 0·1930 Rb_2SO_4. Rb = 30·54.

$RbIO_4$ requires I = 45·9; Rb = 30·91 per cent.

The high value for iodine and the low value for rubidium point to the presence of a small amount of potassium. The salt forms beautiful, colourless, tetragonal crystals, strictly isomorphous with the potassium compound:

Specific gravity at 16°/4° = 3·918. Mol. vol = 70·56.

Solubility: 100 parts of water dissolve 0·65 part at 13°, and the specific gravity of the saturated solution at 16°/4° is 1·0052.

---

* Potassium periodate was stated by Rammelsberg to be orthorhombic and isomorphous with the perchlorate, but, in spite of all efforts, the author did not succeed in obtaining an orthorhombic modification, so he communicated with Prof. Groth, of Munich, who fortunately had in his possession the preparation originally measured by Rammelsberg. Prof. Groth kindly had the crystals analysed, and they were found to contain no trace of iodine, being, in fact, practically pure potassium perchlorate.

Caesium periodate, $CsIO_4$, was first prepared by Wells (*Amer. Chem. J.*, 1901, **26**, 278) by neutralising periodic acid with cæsium carbonate. The salt may also be prepared by the chlorine method, but the yield is by no means good, much iodate precipitating with the crystals of the periodate; the bulk of the author's salt was therefore obtained by Wells's method:

0·4601 gave 0·3321 AgI. I = 39·02.

$CsIO_4$ requires I = 39·20 per cent.

Cæsium periodate is fairly soluble in water, and crystallises in well-defined plates belonging to the orthorhombic system, and is therefore not isomorphous with the potassium and rubidium compounds:

Specific gravity at 15°/4° = 4·259. Mol. vol. = 76·04.

Solubility: 100 parts of water dissolve 2·15 parts at 15°, and the specific gravity of the saturated solution at 15°/4° is 1·0166.

Ammonium periodate, NH_4IO_4, was obtained by neutralising a solution of periodic acid prepared by Wells's method (*loc. cit.*) with aqueous ammonia; the salt is isomorphous with the potassium and rubidium compounds:

Specific gravity at 18°/4° = 3·056. Mol. vol. = 68·39.

Solubility: 100 parts of water dissolve 2·70 parts at 16°, and the specific gravity of the saturated solution at 16°/4° is 1·0178.

Sodium periodate, $NaIO_4$, crystallises in two forms: one anhydrous, isomorphous with the ammonium salt; the other with 3 molecules of water, in the rhombohedral system:

Specific gravities: $NaIO_4$ at 16°/4° = 3·865. Mol. vol. = 55·37.
" $NaIO_4,3aq.$ at 18°/4° = 3·219. Mol. vol. = 83·28.

The periodates of potassium, rubidium, ammonium, sodium, as well as of silver and lithium (according to Rammelsberg) form therefore an isomorphous group, crystallising in the tetragonal system. The group is interesting, not only because the majority of the elements in the first group of the periodic classification are represented, but also because the crystalline form is extraordinarily similar to that of the minerals of the scheelite group. The cause of this is, no doubt, to be found in the similarity of the type of composition, $KIO_4,CaWO_4$, just as it is in certain other pairs of compounds, for example, calcium carbonate and sodium nitrate, and potassium perchlorate and barium sulphate.

The author's thanks are due to Prof. H. A. Miers, in whose laboratory the above work was carried out.

MINERALOGICAL DEPARTMENT,
UNIVERSITY MUSEUM,
OXFORD.

III.—*Acylogens and Thiocarbamides.*

By AUGUSTUS EDWARD DIXON and JOHN TAYLOR.

IT has been shown in previous communications (Dixon and Taylor, Trans., 1907, **91**, 912; see also Dixon and Hawthorne, *ibid.*, 122) that the reaction between certain well-defined acylogens and thiocarbamide, or its aryl monosubstitution derivatives,* leads to the production of halogen salts derived from iminothiocarbamic acid, thus:

(i) $NH_2{\cdot}CS{\cdot}NH_2 + R{\cdot}COCl = HCl + NH_2{\cdot}C(NH){\cdot}S{\cdot}COR$;
(ii) $ArNH{\cdot}CS{\cdot}NH_2 + R{\cdot}COCl = HCl + ArNH{\cdot}C(NH){\cdot}S{\cdot}COR$.

As a rule, salts of class (i) are easily hydrolysed with regeneration of thiocarbamide, but undergo molecular change when heated, the acyl group becoming associated with one of the nitrogen atoms to form an acyl-substituted thiocarbamide:

$$NH_2{\cdot}C(NH){\cdot}S{\cdot}COR,HCl \longrightarrow HCl + RCO{\cdot}NH{\cdot}CS{\cdot}NH_2.$$

Those of class (ii) are distinctly more stable, yielding, by cautious withdrawal of the combined halogen acid in the cold, a substance having the empirical formula of the corresponding base, namely,

$$ArNH{\cdot}C(NH){\cdot}S{\cdot}COR.$$

This substance, however, is not the base, but an isomeride,

$$RCO{\cdot}NAr{\cdot}CS{\cdot}NH_2;$$

the acyl group, as soon as the halogen acid is neutralised, parting from the sulphur to become associated with that nitrogen atom which already holds in combination a hydrocarbon radicle.

Under the influence of heat, or of a dilute alkali (compare Hugershoff, *Ber.*, 1899, **32**, 3649), the first intramolecular movement of the acyl group is followed by a second; this time to the remaining nitrogen atom, where, in the configuration:

---

* Although in many reactions thiocarbamide behaves, not as $CS(NH_2)_2$, but as iminothiocarbamic acid, $NH{:}C(SH){\cdot}NH_2$, and the like is true as regards a large number of its substitution derivatives, yet in the present paper (save where a definitely established structure forbids) they are all represented on the thiocarbamide type, and named accordingly. This usage is adopted, however, not to express any view as to their respective constitutions, but solely to avoid the clumsiness of attaching two or more names and formulæ to a single compound. For instance, the so-called phenylthiocarbamide, $PhNH{\cdot}CS{\cdot}NH_2$, may react as $PhN{:}C(SH){\cdot}NH_2$, or as $PhNH{\cdot}C(SH){:}NH$; possibly, also, as a true thiocarbamide; or it may be a thiocarbamide in the static condition. The *ab*-disubstituted thiocarbamides, it would seem, are capable of reacting in three different forms, according to circumstances; if "the constitution of a compound" is to be inferred from its chemical behaviour, it is not easy to judge, in a case like this, how any save a conventional nomenclature is to be applied.

The present being principally a descriptive paper, the authors desire to confine themselves to the experimental results, and to the above statement of the convention respecting names and formulæ.

$$\mathrm{ArNH{\cdot}CS{\cdot}NH{\cdot}COR},$$

the acyl radicle appears to have reached a position of maximum stability.

These statements outline in a merely approximate way the main results hitherto observed. Deviations of various sorts occur; for example, in certain cases, the benzoyl group, when liberated from the sulphur, moves so readily to the non-substituted nitrogen atom (to form an *ab*-disubstituted thiocarbamide) that, although the existence of an *aa*-form was recognisable (*loc. cit.*) through the characteristic reaction whereby thiocyanic acid is produced,

$$\mathrm{ArNAc{\cdot}CS{\cdot}NH_2 + KOH = KSCN + ArNHAc + H_2O},$$

the movement could not be arrested at the substituted nitrogen atom long enough to permit of the isolation of the *aa*-compound.

On the other hand, in the case of the acyl groups, $\cdot CO_2Me$ and $\cdot CO_2Et$, the electronegative character of which is somewhat feeble, the first transfer from sulphur to nitrogen,

$$\mathrm{PhNH{\cdot}C(NH){\cdot}S{\cdot}CO_2Me \longrightarrow PhN(CO_2Me){\cdot}CS{\cdot}NH_2},$$

is brought about very readily, whilst the second, to produce

$$\mathrm{PhNH{\cdot}CS{\cdot}NH(CO_2Me)},$$

could not be accomplished; a failure the more remarkable, considering that by other means the synthesis of the *ab*-compound presents no difficulty.

It may be noted, too, regarding the behaviour of compounds such as $\mathrm{PhNH{\cdot}C(NH){\cdot}S{\cdot}CO_2R,HCl}$, that it is not a matter of indifference whether the radicle, R, be fatty or benzenoid; for, in the latter case, on the withdrawal by alkali of the combined hydrogen chloride, no *aa*-thiocarbamide, $\mathrm{PhN(CO_2Ar){\cdot}CS{\cdot}NH_2}$, is formed, but, instead, decomposition occurs with production of carbon dioxide, the phenol, ArOH, and phenylthiocarbimide.

Beyond the facts here roughly indicated, our knowledge of the behaviour of acylogens with thiocarbamides does not extend very far; interesting work has lately been carried out on the alkyl-ψ-thiocarbamides, derivatives of the type $\mathrm{NH_2{\cdot}C(NH){\cdot}SAlk}$, but, for the present purpose, it is unnecessary to particularise the conclusions.

In this communication, the writers give the results of an inquiry directed mainly in order to learn (i) the effect of using an acylogen the acid radicle of which contains a second halogen element, and (ii) the behaviour of certain acylogens towards thiocarbamides containing non-aromatic substituting radicles.

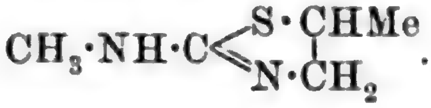
EXPERIMENTAL.

a-Bromopropionyl Bromide and Phenylthiocarbamide.

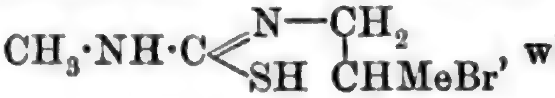
If the reaction between these substances is analogous to that where ordinary alkylogens are concerned, it must proceed primarily as follows:

$$PhNH{\cdot}CS{\cdot}NH_2 + CH_3{\cdot}CHBr{\cdot}COBr = PhNH{\cdot}C(NH){\cdot}S{\cdot}CO{\cdot}CHBr{\cdot}CH_3,HBr.$$

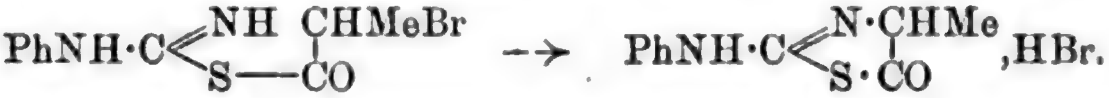
On the other hand, when halogenised radicles are presented for combination with the nitrogen of a thiocarbamide, ring-closing frequently occurs with elimination of halogen acid; thus, for example, Hirsch has shown (*Ber.*, 1890, **23**, 971) that methylthiocarbimide yields with β-bromopropylamine, not the expected methylbromopropylthiocarbamide, $CH_3{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}CH_2{\cdot}CHBr{\cdot}CH_3$, but, instead, the hydrobromide of an isomeric ring-compound,



$$CH_3{\cdot}NH{\cdot}C{<}\begin{matrix}S\cdot CHMe\\ \quad | \\ N\cdot CH_2\end{matrix}.$$

This action may obviously be represented by supposing the thiocarbamide first to be produced, and then to be changed into the labile or tautomeric form,  $CH_3{\cdot}NH{\cdot}C{<}\begin{matrix}N - CH_2\\ \quad\quad | \\ SH\ \ CHMeBr\end{matrix}$, whence, by loss of the elements of hydrogen bromide, the above ring-compound would result.

In like manner, if phenylthiocarbamide were first to yield with a-bromopropionyl bromide the product already formulated, this might easily transform itself into a ring-form, thus:



$$PhNH{\cdot}C{<}\begin{matrix}NH\ \ CHMeBr\\ \quad\quad | \\ S - CO\end{matrix} \longrightarrow PhNH{\cdot}C{<}\begin{matrix}N\cdot CHMe\\ \quad | \\ S\cdot CO\end{matrix},HBr.$$

Experiment gave the results described below.

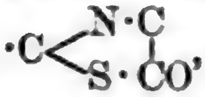
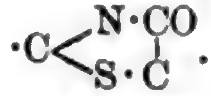
Vigorous action took place on mixing the constituents, dissolved in molecular proportions, in warm acetone, and, on cooling, small, white, glistening plates were deposited, giving with water a clear acid solution. When heated in a narrow tube, the solid darkened slightly at 215°, shrank at 230°, and melted with effervescence and charring at 238—239° (uncorr.).

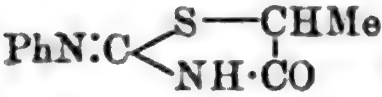
From the solution in water or alcohol, no picrate could be obtained, from which it seemed improbable that a-bromopropionyl-ψ-phenylthiourea hydrobromide, $PhNH{\cdot}C(NH){\cdot}S{\cdot}CO{\cdot}CHBr{\cdot}CH_3,HBr$, had been formed; neither did the solution in concentrated alkali yield any trace of red coloration when acidified and treated with ferric chloride; hence there was no reason to suppose that migration of the acyl group had occurred with production of *aa*-bromopropionylphenylthiocarbamide, $CH_3\cdot CHBr\cdot CO\cdot NPh\cdot CS\cdot NH_2$.

A bromine determination, however, gave figures concordant with the latter formula:

0·368 required 12·75 c.c. *N*/10 silver nitrate. Br = 27·75.

$C_{10}H_{11}ON_2BrS$ requires Br = 27·87 per cent.

But on further examination the compound proved to be a hydrobromide, and, since it was not desulphurised by boiling with an alkaline solution of lead, the sulphur must evidently be held in a closed-ring, which could have only the constitution figured above, namely,  $\cdot C{<}\begin{array}{l}N\cdot C\\ S\cdot CO\end{array}$, or, the alternative form,  $\cdot C{<}\begin{array}{l}N\cdot CO\\ S\cdot C\end{array}$. That the latter of these is correct was shown by the fact that the substance, when boiled with baryta water, gave with hydrochloric acid, ferric chloride, and ammonia the purple reaction characteristic of the thioglycollic acids, and hence contains the typical linking: $\cdot S\cdot CH_2\cdot CO\cdot$.

No indication was observed of the presence of any other product than that described, which was obviously the hydrobromide of one of the various forms of so-called phenylmethylthiohydantoin, probably  $PhN{:}C{<}\begin{array}{l}S\text{—}CHMe\\ NH\cdot CO\end{array}$, otherwise, *N*-phenyl-a-methylthiourantoin (see Dixon, Trans., 1897, **71**, 629, 639).

Therefore, in the circumstances given, when two halogens (one being connected with the CO group of an acyl radicle, and the other a substituent in its hydrocarbon nucleus) are presented simultaneously to the SH group of $PhN{:}C(NH_2)\cdot SH$, the hydrogen of this combines preponderantly, if not exclusively, with the substituent halogen; hence the ring-formation which occurs also must depend mainly, if not altogether, on the union of the halogen of the ·COBr with the hydrogen of an amino- or imino-group.

To ascertain whether temperature may influence either the direction of the primary combination (that is, which halogen unites with the SH-hydrogen) or the fact of ring-closing, the experiment was repeated in a freezing mixture at about − 8°. No substantial difference of any sort was noticed, the sulphur of the product appearing, just as before to be linked solely as ·S·CHMe·.

Chloroacetyl Chloride and Phenylthiocarbamide.

Although, in view of the results described above, there could be little doubt as to how these substances would interact, the experiment was tried, the constituents being mixed in cooled acetone. The white product, a hydrochloride, decomposed at 230° with blackening and intumescence; from its aqueous solution, when neutralised, a white solid crystallised out, having the melting point (177—178°) of "phenylthiohydantoin," and giving the reactions of this compound.

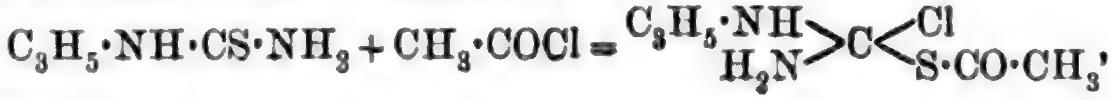
Acetyl Chloride and Allylthiocarbamide.

These substances combined vigorously in presence of acetone, the product, a white, apparently crystalline powder, melting at 103—104° with decomposition and effervescence. Analysis showed it to be a molecular additive compound:

0·389, dissolved in hot ammonia, gave 0·499 Ag_2S, and the filtrate contained 0·2822 AgCl. S = 16·55; Cl = 17·95.

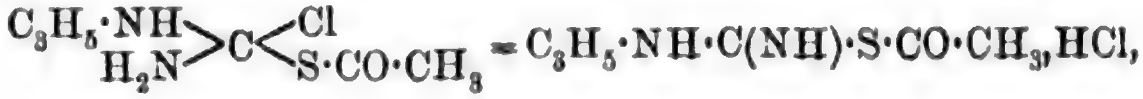
$C_6H_{10}ON_2S,HCl$ requires S = 16·45; Cl = 18·25 per cent.

The interaction may be represented as follows:

(i) 

$$C_3H_5\cdot NH\cdot CS\cdot NH_2 + CH_3\cdot COCl = \begin{matrix}C_3H_5\cdot NH\\ H_2N\end{matrix}\!\!>C<\!\!\begin{matrix}Cl\\ S\cdot CO\cdot CH_3\end{matrix},$$

and then



$$\begin{matrix}C_3H_5\cdot NH\\ H_2N\end{matrix}\!\!>C<\!\!\begin{matrix}Cl\\ S\cdot CO\cdot CH_3\end{matrix} = C_3H_5\cdot NH\cdot C(NH)\cdot S\cdot CO\cdot CH_3,HCl,$$

or

(ii) $C_3H_5\cdot NH\cdot C(NH)\cdot SH + CH_3\cdot COCl =$

$C_3H_5\cdot NH\cdot C(NH)\cdot S\cdot CO\cdot CH_3,HCl.$

Water dissolved the substance very freely, but with considerable decomposition, so that the corresponding *picrate*, an orange-yellow, crystalline solid, could be obtained only in poor yield.

Action of Caustic Alkali.—Twelve grams of the hydrochloride were dissolved in water, and to the solution, without delay, there was run in something less than one equivalent of *N*/3 alkali; the white precipitate was then collected by the aid of the pump. The filtrate, which was strongly acid, required for neutralisation about half an equivalent more of alkali, and now contained both chloride and acetate; consequently, about one-half of the hydrochloride had undergone hydrolysis with regeneration of allylthiocarbamide; no thiocyanate was present.

The crystalline precipitate, free from chlorine, melted at 95—96°, and, when recrystallised from dilute alcohol, formed brilliant needles, showing the same melting point as before. It was now practically insoluble in hydrochloric acid, and its solution in dilute alcohol yielded no picrate; hence the product did not consist of the base: $C_3H_5\cdot NH\cdot C(NH)\cdot S\cdot CO\cdot CH_3$.

It was soluble, however, in dilute alkali, the solution being desulphurised by heating with a lead salt; on the other hand, when heated with strong (30 per cent.) potassium hydroxide, it gave at first a clear solution, which presently became turbid owing to the separation of an oil; the mixture, whilst reacting intensely for thiocyanic acid, was but slightly darkened by boiling with a lead salt, and hence practically all the contained sulphur had been eliminated as thiocyanate, the oil being doubtless allylacetamide. From the above result, it appears that this form of decomposition, so characteristic of the *aa*-acylarylthiocarbamides (see Hugershoff, *Ber.*, 1899, **32**, 3649; compare also Dixon and Hawthorne, Trans., 1907, **91**, 133; Dixon and Taylor, *ibid.*, 916), holds equally in the *aa*-acylalkyl class:

$$C_3H_5\cdot N(CO\cdot CH_3)\cdot CS\cdot NH_2 + KOH = KSCN + H_2O + C_3H_5\cdot NH\cdot CO\cdot CH_3.$$

The above formula was checked by analysis:

0·316 required 40·2 c.c. *N*/10 barium chloride. S = 20·4.
$C_6H_{10}ON_2S$ requires S = 20·25 per cent.

It had now to be learned whether this second form of acetylallylthiocarbamide could be transformed, through migration of the acyl group, into the third, or symmetrical, variety; that such is the case is proved by the result of the following experiment.

Action of Heat.—A quantity of the *aa*-compound was maintained for some time at a temperature between 100° and 105°. After half an hour, the liquid, when treated with caustic alkali, still reacted very strongly for thiocyanic acid, but after some two hours' further heating responded but feebly to the test. On cooling, the brown melt solidified, and the solid, when twice recrystallised from boiling, dilute alcohol, formed long, silky needles melting at 73—74°. With hot water, the product yielded an almost neutral solution, giving no precipitate with excess of picric acid; it was soluble also in cold strong alkali, the solution being desulphurised by boiling with a lead salt, but giving with hydrochloric acid and ferric chloride no trace of red coloration. On analysis:

0·158 gave 0·230 $BaSO_4$. S = 20·0.
$C_6H_{10}ON_2S$ requires S = 20·25 per cent.

This product, accordingly, was isomeric with the last described, and consisted of *ab*-acetylallylthiocarbamide. The series of changes, starting from the compound of allylthiocarbamide and acetyl chloride, may be summed up as follows:

$$C_3H_5\cdot NH\cdot C(NH)\cdot S\cdot CO\cdot CH_3,HCl \longrightarrow C_3H_5\cdot N(CO\cdot CH_3)\cdot CS\cdot NH_2 \longrightarrow C_3H_5\cdot NH\cdot CS\cdot NH\cdot CO\cdot CH_3.$$

When *ab*-acetylallylthiocarbamide was cautiously heated somewhat above its melting point, the pungent odour of acetylthiocarbimide became perceptible, and the fusion, when treated with water and ferric chloride, gave an intense blood-red coloration. This behaviour of acylated thiocarbamides has already been pointed out and discussed (Dixon, Trans., 1906, **89**, 905).

From the foregoing experiments, it may be concluded that when a fatty acylogen reacts with a monosubstituted thiocarbamide the general behaviour of the product, as regards intramolecular movement of the contained acid radicle, is independent of whether the substituting group of the thiocarbamide is cyclic or otherwise. It remained for experiment to show how acetyl chloride would behave with a disubstituted thiocarbamide containing the allyl group.

Acetyl Chloride and ab-*Phenylallylthiocarbamide.*

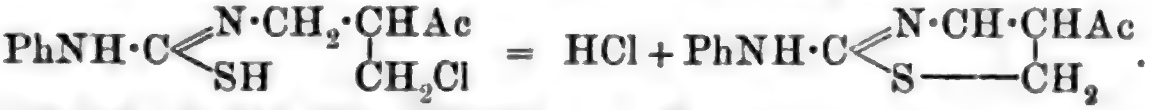
When acetyl chloride was added in slight excess to phenylallylthiocarbamide dissolved in warm benzene, a clear, yellow oil was precipitated, showing even after long keeping no tendency to become solid. The product, a hydrochloride (containing a trace of phenylthiocarbimide), was rather sparingly soluble in water, but easily so in alcohol, the latter solution yielding with alcoholic picric acid a *picrate*, crystallising in long, transparent needles, resembling monoclinic sulphur in colour and appearance, and melting at 154—155° (corr.).

With dilute caustic alkali, the aqueous solution of the hydrochloride gave an oil, soon changing to a crystalline solid; the latter, after two recrystallisations from boiling dilute alcohol, separated in needles melting at 117—118° (corr.). The product was slightly alkaline; when treated with hydrochloric acid, it yielded again the oily hydrochloride, and then in turn the picrate: hence it was plain that the acetyl group, if united originally to sulphur, had not undergone the usual movement to a nitrogen atom, since in that case the basic character would have been lost. Moreover, that the acetyl group had not remained attached to sulphur was evident from the facts, that on boiling the base with caustic alkali and a lead salt the mixture was not darkened, and that the alcoholic solution gave with silver nitrate a white precipitate, sparingly soluble in ammonia and showing no sign of desulphurisation when boiled with it.

Boiling with concentrated nitric acid failed to produce any detectable amount of sulphuric acid; nevertheless the compound contained sulphur, for on ignition with zinc filings, metallic sulphide was obtained, and by fusion with caustic alkali and nitre, alkali sulphate. The sulphur therefore must form part of a ring; from which it was inferred that the acetyl group had probably gone to saturate the allyl group, in which case, ring formation could easily occur in either of the following ways:

(i) $\mathrm{PhNH\cdot CS\cdot NH\cdot CH_2\cdot CH{:}CH_2 + AcCl =}$
$\mathrm{PhNH\cdot CS\cdot NH\cdot CH_2\cdot CHAc\cdot CH_2Cl}$,

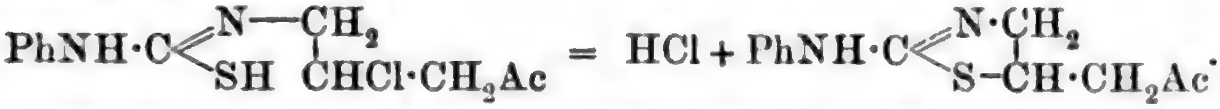
if now, as usual, the chlorine and the SH-hydrogen interact,



$$\mathrm{PhNH\cdot C}{<}\begin{matrix}\mathrm{N\cdot CH_2\cdot CHAc}\\ \mathrm{SH\quad\ \ CH_2Cl}\end{matrix} = \mathrm{HCl + PhNH\cdot C}{<}\begin{matrix}\mathrm{N\cdot CH\cdot CHAc}\\ \mathrm{S{-\!-\!-}CH_2}\end{matrix}.$$

(ii) $\mathrm{PhNH\cdot CS\cdot NH\cdot CH_2\cdot CH{:}CH_2 + AcCl =}$
$\mathrm{PhNH\cdot CS\cdot NH\cdot CH_2\cdot CHCl\cdot CH_2Ac}$;

whence, as before,

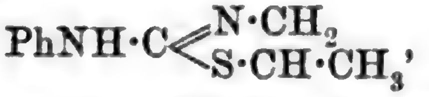


$$\mathrm{PhNH\cdot C}{<}\begin{matrix}\mathrm{N{-\!-}CH_2}\\ \mathrm{SH\quad CHCl\cdot CH_2Ac}\end{matrix} = \mathrm{HCl + PhNH\cdot C}{<}\begin{matrix}\mathrm{N\cdot CH_2}\\ \mathrm{S{-}CH\cdot CH_2Ac}\end{matrix}.$$

Analysis, however, failed to substantiate this view, for:

0·20 gave 24·6 c.c. moist nitrogen at 15° and 748 mm. N = 14·7, whilst the compounds just formulated would require N = 11·97 per cent.

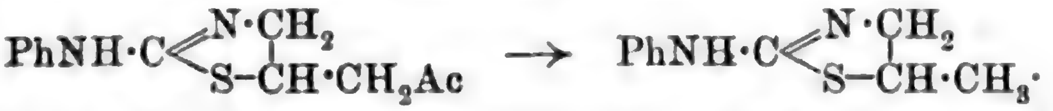
The percentage of nitrogen found agrees closely with that calculated for phenylallylthiocarbamide itself, namely, 14·58, and a comparison of the properties of the product with those of the isomeride of phenylallylthiocarbamide, "*N*-phenylpropylene-ψ-thiourea,"



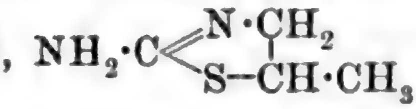
$$\mathrm{PhNH\cdot C}{<}\begin{matrix}\mathrm{N\cdot CH_2}\\ \mathrm{S\cdot CH\cdot CH_3}\end{matrix},$$

obtained by Prager (*Ber.*, 1889, **22**, 2992) from the first-named and concentrated hydrochloric acid at 100°, shows them to be the one compound. Prager gives for the melting points of base and picrate, 117° and 154° respectively; the authors' figures, as stated above, were 117—118° and 154—155°.

If the mechanism of this unexpected change operates as supposed, the chlorine of the acetyl chloride must have united primarily with the middle carbon atom of the allyl group as represented in case (ii) above; here, by the simple exchange of hydrogen for acetyl, however this be conditioned, the propylene configuration would result:



$$\mathrm{PhNH\cdot C}{<}\begin{matrix}\mathrm{N\cdot CH_2}\\ \mathrm{S{-}CH\cdot CH_2Ac}\end{matrix} \rightarrow \mathrm{PhNH\cdot C}{<}\begin{matrix}\mathrm{N\cdot CH_2}\\ \mathrm{S{-}CH\cdot CH_3}\end{matrix}.$$

Considering that allylthiocarbamide reacts with hydrochloric acid at 100° in precisely the same way as does phenylallylthiocarbamide (that is, propylene-ψ-thiourea is formed,  $\mathrm{NH_2\cdot C}{<}\begin{matrix}\mathrm{N\cdot CH_2}\\ \mathrm{S{-}CH\cdot CH_3}\end{matrix}$; see Gabriel, *Ber.*, 1889, **22**, 2985), it seems curious that the two should behave so differently with acetyl chloride.

The question naturally arising whether an acylogen less electronegative than acetyl chloride would behave similarly to the latter, the alkyl chlorocarbonates were selected for the purpose of experiment.

Methyl Chlorocarbonate and Phenylallylthiocarbamide.

Slight excess of methyl chlorocarbonate was added to a gently warmed solution of phenylallylthiocarbamide in acetone. No heat was evolved, nor did the mixture become turbid, but on evaporation at the ordinary temperature, beautiful, large, vitreous prisms were obtained; after being well washed with ether and dried, they melted with copious effervescence at about 87°.

The product dissolved in sulphuric acid with frothing and evolution of hydrogen chloride. On analysis:

0·3006 required 10·5 c.c. *N*/10 silver nitrate. Cl = 12·4.

$C_{12}H_{14}O_2N_2S,HCl$ requires Cl = 12·39 per cent.

About 88 per cent. of the theoretical yield was obtained. The gas expelled by heating the hydrochloride proved to be carbon dioxide; by maintaining the heat cautiously until the effervescence ceased, an oily residue was obtained, the solution of which in water gave with caustic alkali a white, oily precipitate having a strong odour of mercaptan and yielding with a lead salt the yellow lead mercaptide. The chlorocarbonate residue therefore had become attached to the sulphur atom (and not to the allyl group), the change by heat proceeding thus:

$$C_3H_5{\cdot}NH{\cdot}C(N{\cdot}C_6H_5){\cdot}S{\cdot}CO_2{\cdot}CH_3,HCl = CO_2 + C_3H_5{\cdot}NH{\cdot}C(N{\cdot}C_6H_5){\cdot}S{\cdot}CH_3,HCl.$$

Action of Water on the Hydrochloride.—When added to water, the hydrochloride yielded a very acid solution, which, if treated at once with picric acid, gave the bright yellow picrate; with caustic alkali, it furnished a white precipitate, soluble in excess, the solution having a distinct odour of mercaptan, and undergoing desulphurisation when heated with a lead salt. On the other hand, the aqueous solution, when kept for a short time, became turbid (the same change occurred at once on warming), owing to the separation of an oil, soon changing to a crystalline solid; the liquor from this, when treated with picric acid, yielded no precipitate, neither did caustic alkali give any precipitate or produce the odour of mercaptan; when the alkaline mixture was treated with a lead salt, no mercaptide was formed, but desulphurisation occurred on warming:

The material precipitated by the action of water on the dissolved hydrochloride contained no chlorine and had lost all basic properties; it was now insoluble in dilute hydrochloric acid, and did not yield a picrate. When recrystallised from dilute alcohol, it formed long, colourless prisms, melting at 82—83° without effervescence. The solution in caustic alkali gave no mercaptan on heating, and when mixed with a lead salt was slowly desulphurised by boiling.

These phenomena are so nearly in accordance with those observed for the compounds of ethyl chlorocarbonate with phenylthiocarbamide and its congeners (Dixon and Taylor, *loc. cit.*) as to leave no doubt that all belong to the same class.

What occurs therefore in the attack by water may be explained as follows. Dissociation of the hydrochloride takes place, the hydrochloric acid passing into solution with liberation of the free base, either carboxymethyl-ψ-*n*-phenyl-ν-allylthiourea,

$$C_3H_5{\cdot}NH{\cdot}C(NPh){\cdot}S{\cdot}CO_2Me,$$

or its tautomeride, carboxymethyl-ν-phenyl-ψ-*n*-allylthiourea,

$$PhNH{\cdot}C(N{\cdot}C_3H_5){\cdot}S{\cdot}CO_2Me,$$

which is unstable in presence of water, probably by reason of the feeble attraction between sulphur and the acidic group. In a case such as this, at least so far as we yet know, if neither of the nitrogen atoms of the thiourea be substituted, the acid group simply leaves the molecule by hydrolysis, whereupon the corresponding thiocarbamide is regenerated; but if one be substituted, the acyl group now moves to it, and there becomes attached, so as to produce an *aa*-disubstituted thiocarbamide. In this particular instance, where both nitrogen atoms are substituted by different radicles, the acyl group might become attached to either, or distributively to both; it was observed, however, that in the attack by caustic alkali, phenylthiocarbimide was always produced, a fact which gives some clue to the position of the phenyl group. For, when caustic alkali decomposes an *aa*-disubstituted acidic thiocarbamide, the interaction takes place almost quantitatively as follows:

$$AcArN{\cdot}CS{\cdot}NH_2 = AcArNH + HSCN.$$

That is, of the two hydrogen atoms available, one goes to form substituted amide, the other yielding H·NCS, a compound which does not exist as such in contact with water, but passes rapidly into the form, H·SCN. If the behaviour of a trisubstituted derivative is similar, then, when the one remaining hydrogen atom has passed over to the disubstituted nitrogen atom to form the corresponding amide, there remains only CSN·R, a thiocarbimide, the radicle, R, being that originally associated with the hydrogenised nitrogen. Since, then, in the above decomposition, phenylthiocarbimide is produced (no thiocyanic acid could be detected), there is at least some ground for supposing the composition of the parent compound to be:

$$C_3H_5{\cdot}N(CO_2Me){\cdot}CS{\cdot}NH{\cdot}C_6H_5,$$

unless it be the isomeric (or tautomeric) thiourea, from which at present there is no means of distinguishing it.

To check the composition of the supposed trisubstituted derivative, it was analysed:

0·250 gave 0·239 $BaSO_4$. S = 13·1.

$C_{12}H_{14}O_2N_2S$ requires S = 12·80 per cent.

Ethyl Chlorocarbonate and Phenylallylthiocarbamide.

By operating as described in the last case, precisely similar results were obtained, the end product being a crystalline, white hydrochloride, melting with effervescence (due to the escape of carbon dioxide) at 96°:

0·601 required 19·7 c.c. *N*/10 silver nitrate. Cl = 11·6.

$C_{13}H_{16}O_2N_2S,HCl$ requires Cl = 11·81 per cent.

In all respects save one, the properties of this hydrochloride resembled those of the preceding, and hence need not be described in detail. The one point of difference was that the oily precipitate, which separated from the aqueous solution of the hydrochloride, did not solidify, even after remaining for some time at −8° and then for six months in a vacuum desiccator. Otherwise it resembled the methylic homologue, being gradually desulphurised, for example, by hot alkaline lead tartrate, without yielding any odour of mercaptan. Trisubstituted thiocarbamides, containing hydrocarbon groups, are not desulphurised readily, if at all, by this treatment; it is probable therefore that the change mentioned, which is markedly slower than in the case of the parent phenylallylthiocarbamide, is due to the withdrawal of the contained acyl group by means of the alkali.

On analysis, the oil gave the following result:

0·2664 yielded 0·232 $BaSO_4$. S = 12·0.

$C_{13}H_{16}O_2N_2S$ requires S = 12·12 per cent.

Hence it was a form of carboxyethylphenylallylthiocarbamide.

In addition to the above, a number of experiments were conducted with the view of learning whether union could be effected of (1) benzyl chloride with acetylthiocarbamide, and (2) acetyl chloride with benzyl-ψ-thiourea, thus:

$$AcNH{\cdot}CS{\cdot}NH_2 + C_7H_7Cl = AcNH{\cdot}C(NH){\cdot}S{\cdot}C_7H_7,HCl;$$
$$NH_2{\cdot}C(NH){\cdot}S{\cdot}C_7H_7 + AcCl = AcNH{\cdot}C(NH){\cdot}S{\cdot}C_7H_7,HCl,$$

and if so, whether the products would be identical or would differ from one another, owing to the occurrence of tautomeric forms.

Both these combinations, it was found, could easily be effected, the latter occurring vigorously when the constituents, dissolved in cold acetone, were mixed together; in each case, a white, crystalline hydrochloride was isolated, and shown by analysis to be an additive compound. From each hydrochloride, too, a corresponding base was liberated, the sulphur contents of which agreed closely with the figures calculated.

Nevertheless, such considerable variations of melting point were encountered amongst the hydrochlorides that no definite conclusion could be drawn as to their identity or otherwise, and the same was true regarding the bases. The melting points of the latter were generally wanting in sharpness, overlapping one another somewhere in the neighbourhood of 140°; by recrystallisation (during which benzyl mercaptan was freely evolved), they could be made to coincide at 210—211°, the product, acetylcarbamide, resulting, no doubt, from the acetylcyanamide formed by loss of benzyl mercaptan:

$$AcNH{\cdot}C(NH){\cdot}S{\cdot}C_7H_7 = C_7H_7{\cdot}SH + AcNH{\cdot}CN.$$

The compounds being so unstable that there seemed little prospect of isolating them in a really pure condition, the experiments in this direction were not pursued; it may perhaps be added that continued work with benzyl mercaptan is very disagreeable.

With benzylthiocarbamide in acetone, acetyl chloride gave a white hydrochloride, which became pasty even when kept in a desiccator, and had an odour of acetyl chloride. Ferric chloride gave with the aqueous solution no trace of red coloration; but on treatment with strong alkali, thiocyanic acid was produced in abundance, showing that the acetyl group had migrated to the benzylated nitrogen atom. The amount of material being small, no attempt was made to isolate the *aa*-acetylbenzylthiocarbamide. The isomeric *ab*-compound, produced by Werner (Trans., 1891, **59**, 562) from benzylthiocarbamide and acetic anhydride, gives no thiocyanic acid when treated with alkali.

Summary and Conclusion.

Briefly put, the main results of the present inquiry are as follows:

(1) When an ordinary acylogen, R·CO·X (X = halogen), unites with phenylthiocarbamide, the product is a derivative of phenylthiourea, PhNH·C(NH)·SH, having the form:

$$PhNH{\cdot}C(NH){\cdot}S{\cdot}COR.$$

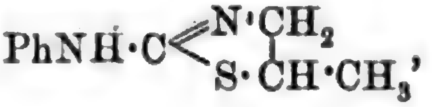
If, however, the acylogen contains a second halogen as substituent in the aliphatic nucleus, R, the interaction takes place differently, the sulphur atom now becoming engaged, not with the carbon of the CO group, but with the other carbon atom which originally was halogenised; concurrently, the halogen of the group ·CO·X withdraws hydrogen from the non-phenylated nitrogen, and ring-closing occurs with production of a substituted "thiohydantoin."

(2) Acetyl chloride behaves with allylthiocarbamide precisely as with monosubstituted arylthiocarbamides, yielding a hydrochloride,

$C_3H_5{\cdot}NH{\cdot}C(NH){\cdot}SAc,HCl$, the acetyl group of which may be caused to migrate within the molecule so as to yield, first,

$$C_3H_5{\cdot}NAc{\cdot}CS{\cdot}NH_2,$$

and then $C_3H_5{\cdot}NH{\cdot}CS{\cdot}NHAc$; the latter compounds melt at 96° and 74° respectively.

(3) With *ab*-phenylallylthiocarbamide, acetyl chloride yields "*N*-phenylpropylene *ψ*-thiourea,"  $PhNH{\cdot}C{<}\begin{matrix}N{\cdot}CH_2\\ S{\cdot}CH{\cdot}CH_3\end{matrix}$, the acetyl group being eliminated.

(4) *ab*-Phenylallylthiocarbamide unites with methyl chlorocarbonate to form a hydrochloride, probably

$$C_3H_5{\cdot}NH{\cdot}C(NPh){\cdot}S{\cdot}CO_2Me,HCl;$$

by mere dissolution in water, this substance loses hydrogen chloride, the carboxymethyl group thereupon migrating to yield a trisubstituted thiocarbamide, probably $C_3H_5{\cdot}N(CO_2Me){\cdot}CS{\cdot}NHPh$. With ethyl chlorocarbonate, similar combinations are obtained.

CHEMICAL DEPARTMENT,
QUEEN'S COLLEGE,
CORK.

IV.—*Condensation of Ketones Containing the Group* $\cdot CH_2{\cdot}CO{\cdot}CH$: *with Esters in Presence of Sodium Ethoxide.*

By REGINALD W. L. CLARKE, ARTHUR LAPWORTH, and ELKAN WECHSLER.

THE acetoacetic ester condensation, in its most general form, is that which occurs when a carboxylic, nitrous, or nitric ester (class E) is brought into contact with a ketone, carboxylic ester, or nitrile (class K) containing the group $\colon CH{\cdot}CO{\cdot}$, or $\colon CH{\cdot}CN$, in presence of sodium ethoxide, sodamide, sodium, or similar agent. The question of its mechanism has been the subject of much controversy and is associated with numerous investigations.[*]

---

[*] Geuther, *Jahresber.*, 1863, 323; *Zeitsch. f. Chem.*, 1868, **11**, 652; Frankland and Duppa, *Phil. Trans.*, 1866, **156**, 37; *Annalen*, 1866, **138**, 204, 328; Kolbe, *Zeitsch. f. Chem.*, 1867, **10**, 637; Wislicenus, *Annalen*, 1877, **186**, 163; Baeyer, *Ber.*, 1885, **18**, 3640; Duisberg, *Ber.*, 1883, **16**, 133; Claisen and Lowman, *Ber.*, 1887, **20**, 651; 1888, **21**, 1154; Brömme and Claisen, *ibid.*, 1888, **21**, 1132; Claisen, *ibid.*, 1894, **27**, 114; 1905, **38**, 708; also *Annalen*, 1893, **277**, 184; 1896, **291**, 25; 1897, **297**, 92; Michael, *J. pr. Chem.*, 1888, [ii], **37**, 507; *Ber.*, 1900, **33**, 3731; 1905, **31**, 1922; Nef, *Annalen*, 1897, **298**, 319; Dieckmann, *Ber.*, 1900, **33**, 2670; Lapworth, Trans., 1901, **79**, 1269; 1902, **81**, 1512; Proc., 1903, **19**, 190.

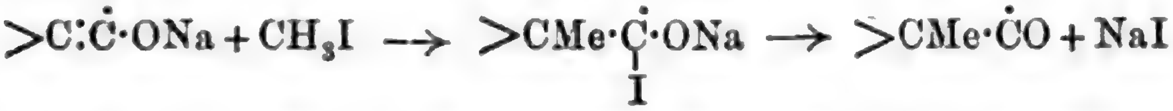
In spite of all evidence against it, Claisen's theory of the mechanism of the condensation (*Ber.*, 1887, **20**, 646; 1888, **21**, 1154) is still the one most frequently cited. The theory was advanced at a time when the general rule appeared to obtain that the substances of class K (above) must contain the group $\cdot CH_2\cdot CO\cdot$, or $CH_2\cdot CN$, and fell to the ground when Dieckmann explained the apparent absence of reactivity in compounds containing the group $⋮CH\cdot CO\cdot$, or $⋮CH\cdot CN$ (*Ber.*, 1900, **33**, 2670), and Perkin and Thorpe discovered a case which could not possibly be explained by Claisen's proposition (Trans., 1900, **79**, 736 and 737).

In the work described in the latter part of the present paper, it is shown that certain simple ketones containing the group

$$⋮CH\cdot CO\cdot CH_2\cdot,$$

when submitted to the action of an alkyl nitrite under the conditions which with other esters lead, as usual, to attack at the $\cdot CH_2\cdot$ group, are affected only at the $⋮CH\cdot$ group, and an explanation of this is afforded readily enough on general grounds and in the light of Dieckmann's experiments. Claisen's theory, however, is not applicable, and in this connexion his own words may be quoted: "Zu verwerfen sind natürlich alle Vorstellungen, mit denen nur einzelne, nicht alle dieser Estercondensationen erklärt werden" (*Ber.*, 1905, **38**, 715).

Other views of the acetoacetic ester condensation have assumed a preliminary conversion of the compounds of class K into their *C*-sodium derivatives, $Na\cdot\underset{\cdot}{\dot{C}}\cdot CO\cdot$, or $Na\cdot\underset{\cdot}{\dot{C}}\cdot CN$ (Frankland and Duppa, *Annalen*, 1883, **219**, 123; Baeyer, *Ber.*, 1885, **18**, 3640; compare also Michael in numerous papers already cited), but recently the tendency has grown among chemists to suppose that the metallic derivatives of ketones, nitriles, &c., when they exist, are derived solely from the enolic forms, and such is doubtless the case with the solid compounds; consequently, efforts have been made to explain the apparently anomalous reactions of these *O*-sodium derivatives as involving additions at the double linking, for example:



$$>C{:}\dot{C}\cdot ONa + CH_3I \longrightarrow >CMe\cdot\underset{\substack{|\\ I}}{\dot{C}}\cdot ONa \longrightarrow >CMe\cdot\dot{C}O + NaI$$

(Michael, *J. pr. Chem.*, 1883, [ii], **27**, 487; 1892, [ii], **46**, 205; 1899, [ii], **60**, 316), or, as the result of isomeric change in pre-formed *O*-substituted compounds:

$$>C{:}\dot{C}\cdot O\cdot CH_3 \longrightarrow >CMe\cdot\dot{C}{:}O$$

(compare Claisen, *Ber.*, 1905, **38**, 714, where such a change is assumed as a part of the mechanism of the acetoacetic ester synthesis).

Serious objections can be urged against such explanations, and we venture here to draw attention once more to what appears likely to prove the most satisfactory view, namely, that isomeric change is involved, but that it is to be looked for in the ions of the metal derivative (Wislicenus, "Tautomerie," Ahrens' *Vorträge*, 897 *et seq*; Knorr, *Annalen*, 1896, **293**, 38; Lapworth and Hann, Trans., 1902, **81**, 1512; 1904, **85**, 48; Lapworth, Proc., 1903, **19**, 190) or in the sodium derivative itself (Lander, Trans., 1903, **83**, 420). It may here be noted that Brühl has brought forward some evidence that metallic derivatives of camphor can actually be isolated in both the *C*- and *O*-forms (*Ber.*, 1904, **37**, 2170).

Apart altogether from the conception of electrolytic dissociation, the exceptional lability of metals, and especially those of the alkalis and alkaline earths as exemplified by the almost universal and instantaneous reactivity of the metallic salts and even organo-metallic compounds, is sufficient to render it likely that they must be more labile than any other types of atoms or groups. Lander's proposition may usefully be employed as an alternative to the earlier ionic one, being especially attractive, since Kahlenberg's experiments with the oleates in which the metals exhibit their instantaneous lability in spite of the absence of noticeable dissociation.

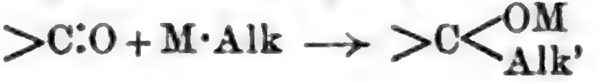
From this standpoint, there is, in solutions of the sodium derivatives of β-ketonic esters and allied compounds, a virtual or real equilibrium between the *O*- and *C*-sodium derivative:

$$\mathrm{\vdots C\vdots \dot{C}ONa} \longleftrightarrow \mathrm{\vdots CNa\cdot\dot{C}O},$$

and this may be at once extended to the metallic derivatives of other compounds containing the groups $\mathrm{\vdots CH\cdot CO\cdot}$, $\mathrm{\vdots CH\cdot CN}$, $\mathrm{\vdots CH\cdot NO_2}$, &c., and, where amines are employed as catalytic agents in promoting condensations with such compounds, then the ammonium radicle, $\mathrm{NR_3H\cdot}$, may be supposed to functionate as a metal. For convenience, however, in the following lines, the univalent metal or ammonium radicle functionating as the positive, labile, "polar" portion (compare Abegg, *Ber.*, 1905, **38**, 4112 *et seq.*) will be represented by the symbol *M*.

The real or virtual existence of *C*-metallic derivatives of the compounds of class K (see p. 30) having been postulated, a satisfactory explanation of the acetoacetic ester condensation, as well as of a large number of other reactions which occur with the compounds of class K in alkaline media, follows without difficulty. The *C*-metallic derivatives should exhibit the characters of organometallic compounds proper, and a little consideration of the facts shows this to be the case, for the reactions of the metallic derivatives of ketones, and class K generally, are either those of phenols (enols) or of organo-metallic compounds, although, in the latter instance, developed to a less marked degree owing to their lower potential consequent on the more "negative" character of the organo-radicle (Michael).

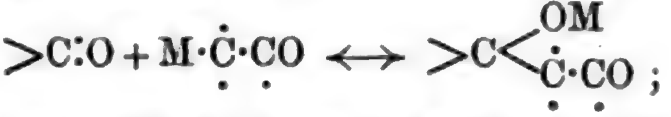
In the present instance, the question under consideration is that of the reactions of the isomeric *M*-derivatives with carbonyl and cyano-groups. Organo-metallic compounds proper are characterised by the extraordinary facility with which they form additive compounds with substances containing the carbonyl group:



$$>\mathrm{C{:}O}+\mathrm{M{\cdot}Alk}\longrightarrow\ >\mathrm{C}<^{\mathrm{OM}}_{\mathrm{Alk}},$$

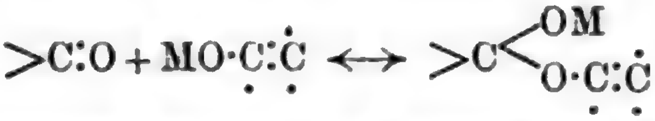
and analogous compounds are formed by addition to $\cdot CN$, $\cdot SO_2\cdot$, $\cdot N{:}O$ groups.

The *C*-metallic derivatives of ketones, esters, nitriles, and nitro-paraffins behave in the same way:



$$>\mathrm{C{:}O}+\mathrm{M{\cdot}}\underset{\cdot\ \cdot}{\dot{\mathrm{C}}}\mathrm{{\cdot}CO}\longleftrightarrow\ >\mathrm{C}<^{\mathrm{OM}}_{\underset{\cdot\ \cdot}{\dot{\mathrm{C}}}\mathrm{{\cdot}CO}}\ ;$$

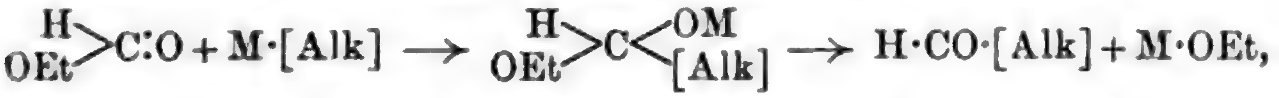
the change, when it ceases here, being known as the aldol condensation, and being to some extent reversible. The carbonyl compound $>C{:}O$ virtually selects the *C*-metallic derivative rather than the *O*-derivative, but merely because the products of its condensation with the latter:



$$>\mathrm{C{:}O}+\mathrm{MO{\cdot}C{:}}\underset{\cdot\ \cdot}{\dot{\mathrm{C}}}\longleftrightarrow\ >\mathrm{C}<^{\mathrm{OM}}_{\mathrm{O{\cdot}C{:}}\underset{\cdot\ \cdot}{\dot{\mathrm{C}}}}$$

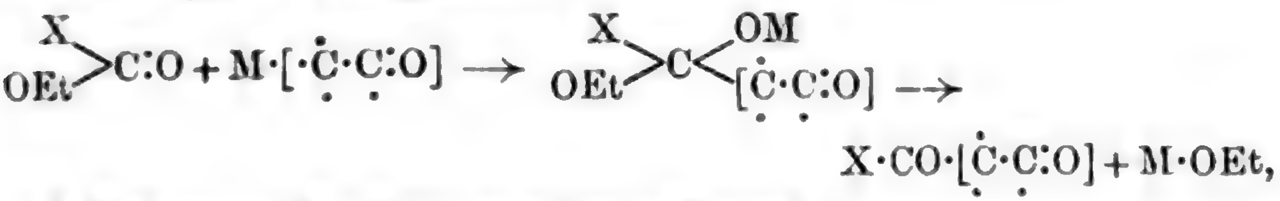
are of a type eminently unstable and revert at once to their generators. The aldol condensation when brought about by bases may thus itself be regarded as an instance of the general reaction between organo-metallic compounds and substances of class K, and, moreover, is recognised as a necessary stage in a very large number of reactions to which special names have been attached, such as the croton-aldehyde condensation, the Perkin synthesis, and others.

The acetoacetic ester condensation is also clearly only a particular case of the interaction of esters and organo-metallic compounds. Thus one of the latter acting on ethyl formate yields an aldehyde:



$${}^{\mathrm{H}}_{\mathrm{OEt}}>\mathrm{C{:}O}+\mathrm{M{\cdot}[Alk]}\longrightarrow{}^{\mathrm{H}}_{\mathrm{OEt}}>\mathrm{C}<^{\mathrm{OM}}_{\mathrm{[Alk]}}\longrightarrow\mathrm{H{\cdot}CO{\cdot}[Alk]}+\mathrm{M{\cdot}OEt},$$

whilst with the *C*-metallic derivative of a carbonyl compound precisely the same type of change occurs:

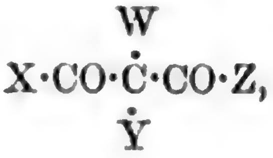


$${}^{\mathrm{X}}_{\mathrm{OEt}}>\mathrm{C{:}O}+\mathrm{M{\cdot}[{\cdot}}\underset{\cdot\ \cdot}{\dot{\mathrm{C}}}\mathrm{{\cdot}C{:}O]}\longrightarrow{}^{\mathrm{X}}_{\mathrm{OEt}}>\mathrm{C}<^{\mathrm{OM}}_{[\underset{\cdot\ \cdot}{\dot{\mathrm{C}}}\mathrm{{\cdot}C{:}O]}}\longrightarrow\mathrm{X{\cdot}CO{\cdot}[}\underset{\cdot\ \cdot}{\dot{\mathrm{C}}}\mathrm{{\cdot}C{:}O]}+\mathrm{M{\cdot}OEt},$$

a β-diketone or β-ketonic ester being formed.

Confusion has probably arisen simply because the product in the latter instance is, from its very nature, prone to further change, but the substances isolated are exactly those which the compound $X\cdot CO\cdot\underset{\cdot}{\dot{C}}\cdot\underset{\cdot}{C}\colon O$ would yield under the experimental conditions. With the latter point, Dieckmann has already dealt (*loc. cit.*), and reference may be made to his paper, but the following forms a very brief summary of the possibilities.

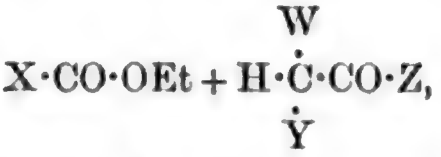
Representing the above condensation product as



$$X\cdot CO\cdot\overset{W}{\underset{Y}{C}}\cdot CO\cdot Z,$$

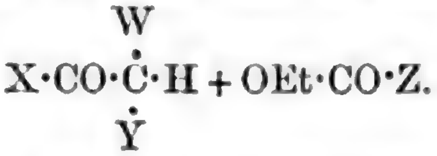
then

1. (*a*) If X, W, Y, and Z are all alkyl groups, the compound is unstable under the experimental conditions, and falls into its generators:



$$X\cdot CO\cdot OEt + H\cdot\overset{W}{\underset{Y}{C}}\cdot CO\cdot Z,$$

by reversal, or (*b*) might break up into two new compounds:



$$X\cdot CO\cdot\overset{W}{\underset{Y}{C}}\cdot H + OEt\cdot CO\cdot Z.$$

2. If either W or Y is a hydrogen atom, then the substance is converted by the metallic alkyl oxide into a stable metallic derivative of the enolic form, reversal thus being obviated.

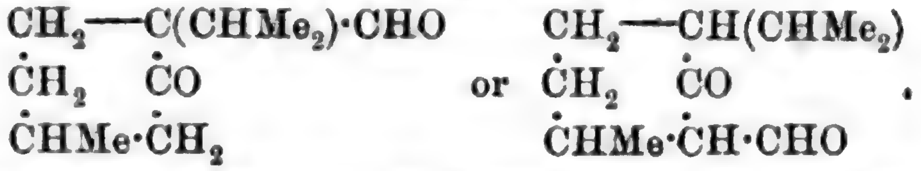
3. If Z (or X?) has the structure $\cdot CHR\cdot CO\cdot R'$ or $\cdot CHR\cdot CN$, then, even if W and Y are both alkyl groups, a stable metal enolic derivative may be formed and reversal inhibited.

Case 1 (*a*) has been dealt with by Dieckmann (*loc. cit.*), but case 1 (*b*) has not yet been observed. Case 2 is the ordinary acetoacetic ester type of synthesis so fully elaborated by Claisen. Case 3 is that noticed by Perkin and Thorpe (Trans., 1900, **79**, 736 and 737).

The condensations dealt with in the present paper were made with ketones containing the groups $\cdot CH_2\cdot CO\cdot\underset{\cdot}{\dot{C}}H$ and $CH_2\cdot CO\cdot\dot{C}\colon\underset{\cdot}{\dot{C}}$ respecttively, the ester with which they were made to react being a nitrous and not a carboxylic ester. It has usually been supposed that, as with other esters, these condense only with ketones which contain the group $\cdot CH_2\cdot CO\cdot$, but such is, in reality, not the case. In the instances we have examined, attack appears to be directed almost exclusively at the $\vdots CH\cdot CO\cdot$ group.

The behaviour of menthone with alkyl formates, on the one hand,

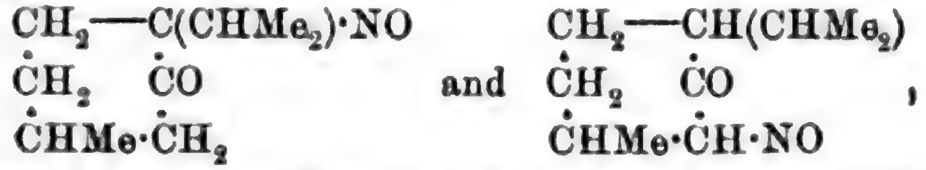
and alkyl nitrites, on the other, is very instructive. In the former instance, the initial products may be either



$$\begin{array}{lll} CH_2\text{—}C(CHMe_2)\cdot CHO & & CH_2\text{—}CH(CHMe_2) \\ \dot{C}H_2 \quad \dot{C}O & \text{or} & \dot{C}H_2 \quad \dot{C}O \\ \dot{C}HMe\cdot\dot{C}H_2 & & \dot{C}HMe\cdot\dot{C}H\cdot CHO \end{array} .$$

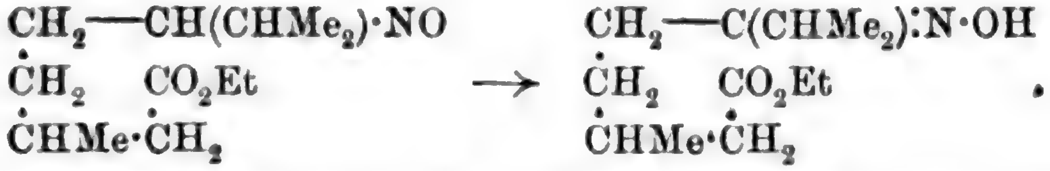
Of these, the former is perhaps formed more rapidly than the other at first, but belongs to a highly unstable type and readily falls into its generators, yielding, by absorption of alcohol, alkyl formate and menthone. The latter, however, is rendered stable by conversion into the sodium derivative of the enolic form, which the former cannot yield.

With alkyl nitrite, the corresponding forms are:



$$\begin{array}{lll} CH_2\text{—}C(CHMe_2)\cdot NO & & CH_2\text{—}CH(CHMe_2) \\ \dot{C}H_2 \quad \dot{C}O & \text{and} & \dot{C}H_2 \quad \dot{C}O \\ \dot{C}HMe\cdot\dot{C}H_2 & & \dot{C}HMe\cdot\dot{C}H\cdot NO \end{array} ,$$

and here the former type does not revert to its generators, owing no doubt to the greater stability of the linking $\cdot\underset{\bullet}{\overset{\bullet}{C}}\cdot NO$ compared with $\cdot\underset{\bullet}{\overset{\bullet}{C}}\cdot CO\cdot$. As a result, it is at the grouping $\cdot\underset{\bullet}{C}\cdot CO\cdot$ that re-absorption of the elements of alcohol occurs, and the next products in succession are:

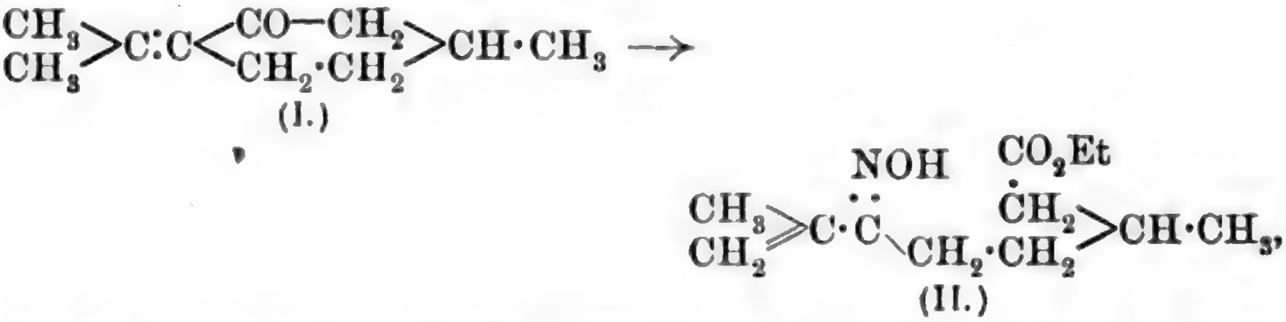


$$\begin{array}{lll} CH_2\text{—}CH(CHMe_2)\cdot NO & & CH_2\text{—}C(CHMe_2)\!:\!N\cdot OH \\ \dot{C}H_2 \quad CO_2Et & \longrightarrow & \dot{C}H_2 \quad CO_2Et \\ \dot{C}HMe\cdot\dot{C}H_2 & & \dot{C}HMe\cdot\dot{C}H_2 \end{array} .$$

The compound obtained as the product of the reaction, on removing alcohol, neutralising, and extracting, has the properties of an ester, and this, if boiled with alkalis, is converted into the same hydroximino-acid as is obtained by treatment of menthone with amyl nitrite and hydrochloric acid, but the yield in the latter instance is comparatively very poor.

The first observation of this apparently anomalous behaviour of nitrous esters when used in conjunction with sodium ethoxide was made by Hantzsch (*Ber.*, 1887, **20**, 579; compare also Dieckmann, *Ber.*, 1900, **33**, 579), but referred to α-monosubstituted β-ketonic esters, and he does not attribute any special significance to his results, probably because such compounds are resolved in so many different ways at the point between the α- and β-carbon atoms. The compounds dealt with in the present paper are simple ketones, and the investigation was undertaken with the object of finding an explanation of the results obtained when an attempt was made to prepare *iso*nitrosocyanodihydrocarvone (Lapworth and Wechsler, Trans., 1907, **91**, 978 and 1919). Here we were forced to the conclusion that attack took place, not at the $\cdot CH_2\cdot CO\cdot$ group, but exclusively at the $\because CH\cdot CO\cdot$ complex.

From pulegone (I), by similar treatment, we obtained an ester having the structure (II):

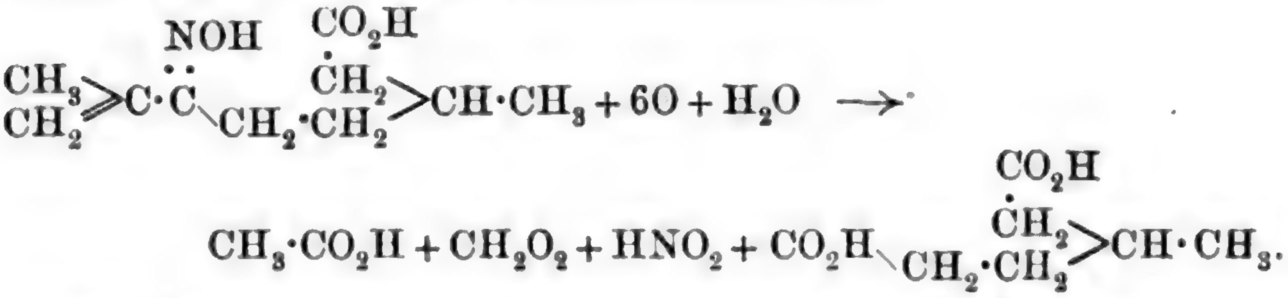


(I.)

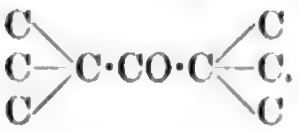
(II.)

so that a migration of a hydrogen atom from the side-chain to the α-carbon atom must have occurred at an intermediate stage; in other words, a partial conversion of pulegone into *iso*pulegone seems to have taken place.

The constitution of the product was determined by oxidising the acid with permanganate, when it was found to be converted into formic, acetic, nitrous, and β-methyladipic acids:



Other compounds examined in respect to their behaviour with nitrous esters and sodium ethoxide were α-bromocamphor, $C_8H_{14}<\begin{matrix}CHBr\\ |\\ CO\end{matrix}$, which reacted readily, but yielded ordinary *iso*nitrosocamphor, and fenchone which was unchanged, although a variety of conditions was imposed, and thus further support is offered to the contention of Semmler (*Ber.*, 1906, **39**, 2581) that fenchone contains the grouping



EXPERIMENTAL.

Action of Amyl Nitrite on Menthone in Presence of Sodium Ethoxide.

In the first experiments on this reaction, it was found that an oily substance only was obtained if the product was isolated merely by dilution and extraction with solvents. This oily material, it was noticed, evolved a considerable quantity of amyl alcohol when treated with alkalis or acids, and this led to the surmise that esters were present, so that the following process was adopted.

Menthone was added to an ice-cold solution of slightly more than one atomic proportion of sodium in absolute alcohol, and subsequently a molecular proportion of amyl nitrite was introduced at such a rate that the temperature did not rise more than one or two degrees above zero. After standing in the cold for some hours, the whole was distilled with the aid of a current of steam until the distillate was odourless, the resulting liquid being then agitated with a little animal charcoal and filtered. Hydrochloric acid was next added to the cooled solution until no further precipitate formed, the oily substance which separated being allowed to solidify, when it was removed and crystallised from methyl alcohol. In this way, 75 grams were obtained in a nearly pure state from 85 grams of menthone:

0·3102 gave 0·6738 CO_2 and 0·2644 H_2O. C = 59·3; H = 9·5.

0·2153 „ 15·45 c.c. moist nitrogen at 14° and 746 mm. N = 7·1.

$C_{10}H_{19}O_3N$ requires C = 59·7; H = 9·5; N = 7·0 per cent.

0·961 required 47·1 c.c. $N/10$ NaOH for neutralisation, whence the equivalent = 204 (calculated = 201).

As the properties of the acid agreed closely with those of the oxime of $\beta\zeta$-dimethyloctan-ϵ-onoic acid, obtained by the action of amyl nitrite on menthone in presence of acid as catalyst, some of that oxime was prepared by the latter process. No difference between the two substances could be detected, and their melting points were unaltered on admixture. The following new derivatives of the acid were prepared.

The p-*nitrophenylhydrazone* formed a bright yellow, crystalline powder melting at 130°:

0·1059 gave 11·9 c.c. moist nitrogen at 16° and 758 mm. N = 13·1.

$C_{16}H_{25}O_5N_3$ requires N = 13·1 per cent.

The *semicarbazone* was obtained in small, white crystals:

0·1208 gave 18·1 c.c. moist nitrogen at 15° and 773 mm. N = 17·8.

$C_{11}H_{21}O_3N_3$ requires N = 17·3 per cent.

These compounds were formed on warming the oxime with aqueous solution, *p*-nitrophenylhydrazine acetate, and semicarbazide acetate respectively, the hydroxylamine being eliminated with great ease.

Action of Amyl Nitrite on Pulegone in Presence of Sodium Ethoxide.

This reaction was carried out in a manner similar to that described in the case of menthone, but, as the esters formed appeared to be more stable, the product, some hours before the steam distillation, was mixed with an excess of strong aqueous potassium hydroxide. The material which separated on acidifying the aqueous residue at the end of the steam distillation was very gummy, and it was found necessary to purify it by dissolving it in ether and extracting the acidic matter from this by shaking it with sodium carbonate solution. After dissolved ether was removed from the alkaline liquid, hydrochloric acid precipitated a viscid mass, which slowly became semicrystalline after trituration with acetic acid. The solid portion was the *oxime* of a new acid, which we propose to term "iso*pulegonic acid*," in order to indicate its near relationship to *iso*pulegone. It was finally purified by crystallisation from dilute methyl alcohol:

0·2070 gave 0·4604 CO_2 and 0·1646 H_2O. C = 60·7; H = 8·8.
0·1538 ,, 9·9 c.c. moist nitrogen at 18° and 738 mm. N = 7·2.
$C_{10}H_{17}O_3N$ requires C = 60·3; H = 8·5; N = 7·0 per cent.

0·4115 required 20·5 c.c. *N*/10 NaOH for neutralisation, whence the equivalent = 201 (calculated = 199).

The compound is readily soluble in methyl or ethyl alcohol, ether, benzene, chloroform, ethyl acetate, or carbon disulphide, but dissolves only sparingly in light petroleum or hot water. It melts at 85°. When heated above its melting point, the compound decomposed, ammonia and an unpleasant smelling vapour being evolved. It reduces a hot ammoniacal solution of silver nitrate, but has no effect on Fehling's solution unless it has been previously heated with a mineral acid, when the product reduces this solution in the cold, a behaviour which indicates that the substance is the oxime of a ketonic acid. The compound gave no crystallisable compound on acetylation. Attempts to obtain a specimen of the pure ketonic acid in a state suitable for analysis were unsuccessful. When it was warmed with hydrochloric acid, the product cooled, and extracted with ether, an oil was removed in small quantity in which the presence of a ketonic acid was proved by warming it with aqueous semicarbazide acetate. The *semicarbazone* separated as a white solid, and, after repeated crystallisation from alcohol, melted at 160°:

0·1060 gave 15·2 c.c. moist nitrogen at 9° and 757 mm. N = 17·2.
$C_{10}H_{16}O_2N\cdot NH\cdot CO\cdot NH_2$ requires N = 17·4 per cent.

Unlike the allied oxime of $\beta\zeta$-dimethyloctan-ϵ-onoic acid, the hydroximino-acid from pulegone is too stable to yield the semicarbazone or *p*-nitrophenylhydrazone when merely warmed with the acetates of the corresponding bases.

Oxidation of the Oxime of iso*Pulegonic Acid.*

As it was found impracticable to isolate pure pulegonic acid, the experiment of oxidising the pure oxime itself was undertaken. Twelve grams of that compound were dissolved in a solution of sodium carbonate, and to the ice-cold solution was added very gradually a 2 per cent. solution of potassium permanganate. The colour of the latter at first disappeared instantaneously, and the addition of the oxidising agent was continued until an appreciable interval elapsed between its introduction and the disappearance of the pink colour, which was the case when about 1½ litres had been used. The liquid was then freed from manganese dioxide in the usual manner, evaporated to a bulk of about 100 c.c., mixed with carbamide, acidified with sulphuric acid, and distilled in a current of steam.

(*a*). *Volatile Acid Products.*—The odour of fatty acids being perceptible, three-fourths of the distillate was neutralised with normal sodium hydroxide, mixed with the remaining fourth, and the whole evaporated. The residue had the appearance of sodium acetate, and gave an ester having the odour of ethyl acetate on treatment with sulphuric acid and alcohol; it was therefore redissolved in water, mixed with silver nitrate solution, and the silver salt which separated was washed, dried, and analysed:

0·3066 gave 0·1981 Ag, whence the equivalent of the volatile acid was 60·1, the equivalent of acetic acid being 62.

The solution from which the silver salt had been removed blackened considerably on standing, a fact indicating the presence of a small quantity of formic acid.

(*b*). *Non-volatile Products.*—The liquid from which the volatile acids had been removed was acidified, extracted repeatedly with ether, which was afterwards washed with a little water, dried, and evaporated, the residue being freed from alcohol by frequent evaporations with water. A semi-solid mass was finally left which was found to yield a considerable quantity of a sparingly soluble copper salt, and the whole was therefore dissolved in water, neutralised with ammonia, and mixed with copper acetate, the precipitated copper salt being removed, washed with water, and decomposed with hydrogen sulphide in the usual way. In this manner, a semicrystalline material was obtained which was freed from adherent oil and crystallised repeatedly from ethyl chloride and light petroleum:

0·1511 gave 0·2920 CO_2 and 0·1047 H_2O. C = 52·7; H = 7·7.
$C_7H_{12}O_4$ requires C = 52·5; H = 7·5 per cent.

0·1232 required 15·7 c.c. *N*/10 NaOH for neutralisation, whence the equivalent = 78·4, whilst a dibasic acid, $C_7H_{12}O_4$, has the equivalent 80·0.

The substance was readily soluble in most of the organic solvents with the exception of light petroleum, and separated in slender needles melting at 84—85°. It did not yield an anhydride when heated at 200°, and had all the characters of β-methyladipic acid.

To confirm the production of formic acid during the above oxidation a specimen of the pure oxime of *iso*pulegonic acid was boiled with dilute sulphuric acid and potassium dichromate, and the distillate, which had a faint odour of formaldehyde, collected. The presence of formaldehyde was confirmed by adding hydrochloric acid and phloroglucinol to a portion of the liquid, when a pink colour developed. The remainder of the distillate was neutralised with sodium carbonate, evaporated, and tested for formate with ammoniacal silver nitrate and with mercuric chloride, and in both cases a positive result was obtained.

No appreciable quantities of products other than nitrous, formic, acetic and β-methyladipic acids could be detected as oxidation products.

Action of Amyl Nitrite on α-Bromocamphor in Presence of Sodium Ethoxide.

When α-bromocamphor was subjected to treatment in the manner described in the case of menthone, rapid action occurred, and potassium bromide separated in considerable quantities. The product was distilled in a current of steam, when much unchanged bromocamphor passed over, and the residue, which was yellow, gave a solid precipitate on neutralisation. This was collected and crystallised from alcohol, when it was found to melt at 152—154°; it was insoluble in solutions of alkali carbonates, although freely soluble in sodium hydroxide, and was therefore not a carboxylic acid. It contained nitrogen, gave camphorquinone when boiled with formaldehyde and hydrochloric acid, and had all the other characteristics of ordinary *iso*nitrosocamphor.

Fenchone did not react with alkyl nitrites under the conditions adopted in any of the experiments above described.

Much of the cost of the investigation was defrayed by a grant awarded by the Research Fund Committee of the Chemical Society, for which we wish to express our indebtedness.

Chemical Department,
Goldsmiths' College,
New Cross, S.E.

V.—*The Electrometric Determination of the Hydrolysis of Salts.*

By Henry George Denham, M.A., M.Sc., 1851 Exhibition Scholar,
University of New Zealand.

Introduction.

Numerous methods have been employed for measuring the amount of hydrolysis in salt solutions. Amongst the most important of these may be mentioned those depending on the determination of the inversion of sucrose, the hydrolysis of methyl acetate, electrical conductivity, lowering of freezing point, and distribution between two solvents. These methods have been employed in the researches of Ley (*Zeitsch. physikal. Chem.*, 1899, **30**, 193); Bruner (*Zeitsch. physikal. Chem.*, 1900, **32**, 133); Walker and Aston (Trans., 1895, **67**, 576); Bredig (*Zeitsch. physikal. Chem.*, 1894, **13**, 289); Kahlenberg, Davis, and Fowler (*J. Amer. Chem. Soc.*, 1899, **21**, 1), and Carrara and Vespignani (*Gazzetta*, 1900, **30**, ii, 35.

None of these methods is really satisfactory for the measurement of very small concentrations of hydrogen ions, and, although Bredig and Fraenkel (*Zeitsch. Elektrochem.*, 1905, **11**, 525) have recently described a new method whereby concentrations of hydrogen ions down to $N/1000$ can be accurately determined, nevertheless the presence of neutral salts produces a disturbing effect, thus rendering the practical applicability of the method rather difficult.

In the present paper, the hydrogen electrode has been used for the purpose of determining the concentration of the hydrogen ions in aqueous salt solutions. This method is particularly suitable when we are dealing with very small concentrations, and it therefore promised to be very useful in many cases when the methods hitherto employed become difficult of application. It suffers, however, from the disadvantage that it cannot be employed in the case of the salts of metals less "noble" than hydrogen, nor in the case of multivalent cations (such as $Fe^{\cdot\cdot\cdot}$) which are reduced by hydrogen to cations of smaller electrovalency, nor is the method admissible in the case of salts with reducible anions as NO_3', ClO_3'. During the course of this work, papers have been published by Bjerrum, in which the same method has been employed in the study of solutions of chromium chloride. Reference will be made to these later.

The Equilibrium Equations of Progressive Salt Hydrolysis.

In dealing with the salts of multivalent cations, the hydrolysis may occur progressively in several stages, to each of which correspond definite equilibria. If aluminium chloride is taken as an example, the progressive stages of the hydrolysis may be represented by the three following purely stoichiometric equations:

$$\mathrm{AlCl_3 + H_2O = AlCl_2(OH) + HCl} \quad \ldots \ldots \quad (1)$$
$$\mathrm{AlCl_3 + 2H_2O = AlCl(OH)_2 + 2HCl} \quad \ldots \ldots \quad (2)$$
$$\mathrm{AlCl_3 + 3H_2O = Al(OH)_3 + 3HCl} \quad \ldots \ldots \quad (3)$$

The mechanism of equation (1) may be represented by the two ionic equilibria:

$$\mathrm{(AlCl_2)^{\cdot} + OH' \rightleftarrows AlCl_2(OH)} \quad \ldots \ldots \quad (1a)$$
$$\mathrm{H^{\cdot} + OH' \rightleftarrows H_2O} \quad \ldots \ldots \quad (4)$$

which may be combined in the simple equilibrium equation:

$$\mathrm{(AlCl_2)^{\cdot} + H_2O \rightleftarrows AlCl_2(OH) + H^{\cdot}} \quad \ldots \ldots \quad (1b)$$

Denoting molar concentrations by square brackets, we have from (1*a*) and (4):

$$[\mathrm{AlCl_2^{\cdot}}].[\mathrm{OH'}] = k_{b_1}[\mathrm{AlCl_2(OH)}] \quad \ldots \ldots \quad (5)$$
$$[\mathrm{H^{\cdot}}].[\mathrm{OH'}] = K_w \quad \ldots \ldots \quad (6)$$

and therefore

$$[\mathrm{AlCl_2^{\cdot}}] = \frac{k_{b_1}}{K_w}[\mathrm{AlCl_2(OH)}][\mathrm{H^{\cdot}}] \quad \ldots \ldots \quad (7).$$

If we now make the simplifying assumptions that aluminium chloride and hydrochloric acid are completely ionised according to the equations:

$$\mathrm{AlCl_3 \rightleftarrows AlCl_2^{\cdot} + Cl'},$$
$$\mathrm{HCl \rightleftarrows H^{\cdot} + Cl'},$$

and if v denotes the molar dilution of the "total" aluminium chloride (hydrolysed and non-hydrolysed), and x the fractional amount hydrolysed, it follows from the above equations and assumptions that

$$[\mathrm{AlCl_2^{\cdot}}] = \frac{1-x}{v},\ [\mathrm{H^{\cdot}}] = [\mathrm{AlCl_2(OH)}] = \frac{x}{v},$$

whence from (7) we have

$$\frac{x^2}{(1-x)v} = \frac{K_w}{k_{b_1}} = K_1 \quad \ldots \ldots \quad (8).$$

It must be observed that x denotes the fractional amount of hydrolysis according to the first stage (equation 1), and that the validity of the equations, $[H^{\cdot}]=[AlCl_2(OH)]=\frac{x}{v}$, depends on the usually made assumption that the value of $[H^{\cdot}]$ is very considerably greater than the value corresponding to the dissociation of pure water.

This "first-stage" hydrolysis is due to the formation of the relatively undissociated basic salt, $AlCl_2(OH)$, which may be regarded as the hydroxide of the complex cation $(AlCl_2^{\cdot})$.

Let us now imagine a state of affairs wherein the hydrolysis corresponds to the stoichiometric equation (2), that is to say, to the formation of the relatively undissociated basic salt, $AlCl(OH)_2$.

Regarding the latter as the hydroxide of the complex cation $AlCl^{\cdot\cdot}$, we might suppose that the second-stage hydrolysis would correspond to more dilute solutions, wherein the dissociation of the aluminium chloride would proceed chiefly or largely according to the equation :

$$AlCl_3 \rightleftarrows AlCl^{\cdot\cdot} + 2Cl''.$$

Assuming that the dissociation of the aluminium chloride according to this equation is complex, and denoting by x the fractional amount of hydrolysis according to equation (2), we obtain

$$[AlCl^{\cdot\cdot}]=\frac{1-x}{v},\ [AlCl(OH)_2]=\frac{x}{v},\ [H\ ]=\frac{2x}{v}.$$

The second-stage hydrolysis being controlled by the equilibrium :

$$AlCl^{\cdot\cdot}+2(OH)' \rightleftarrows AlCl(OH)_2 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (9)$$

together with (6), yields the equations :

$$[AlCl^{\cdot\cdot}][OH']^2=k_{b_2}[AlCl(OH)_2] \text{ and}$$

$$[AlCl^{\cdot\cdot}]=\frac{k_{b_2}}{K_w^2}.[AlCl(OH)_2].[H^{\cdot}]^2,$$

which, on the above assumptions, gives

$$\frac{x^3}{(1-x)v^2}=\frac{K_w^2}{4k_{b_2}}=K_2 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (10).$$

The third-stage hydrolysis corresponding to the stoichiometric equation (3) may be dealt with in a similar way. Assuming complete dissociation of aluminium chloride according to the equation

$$AlCl_3 \rightleftarrows Al^{\cdot\cdot\cdot}+3Cl',$$

and a hydrolysis controlled by the dissociation equilibrium :

$$Al^{\cdot\cdot\cdot}+3OH' \rightleftarrows Al(OH)_3,$$

we have

$$[Al^{\cdot\cdot\cdot}].[OH']^3=k_{b_3}[Al(OH)_3]$$

$$[Al^{\cdot\cdot\cdot}]=\frac{k_{b_3}}{K_w^3}[Al(OH)_3].[H^{\cdot}]^3,$$

and therefore, since $[Al^{\cdot\cdot\cdot}] = \frac{1-x}{v}$, $[Al(OH)_3] = \frac{x}{v}$, and $[H^{\cdot}] = \frac{3x}{v}$,

$$\frac{x^4}{(1-x)v^3} = \frac{K_w{}^3}{27k_{b_3}} = K_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11).$$

For a chloride of a bivalent cation, the first-stage hydrolysis corresponds to equation (8), and the second stage to equation (10).

In the case of a sulphate of a tervalent cation, such as aluminium, the stoichiometric equations representing the progressive hydrolysis are:

$$Al_2(SO_4)_3 + 2H_2O = Al_2(SO_4)_2(OH)_2 + H_2SO_4,$$
$$Al_2(SO_4)_3 + 4H_2O = Al_2(SO_4)(OH)_4 + 2H_2SO_4,$$
$$Al_2(SO_4)_3 + 6H_2O = Al_2(OH)_6 + 3H_2SO_4.$$

Corresponding to the first of these equations, we have the dissociation equilibrium:

$$Al_2(SO_4)^{\cdot\cdot} + 2OH' \rightleftarrows Al_2(SO_4)_2(OH)_2,$$

which leads to

$$[Al_2(SO_4)^{\cdot\cdot}] \, . \, [OH']^2 = k_{b_1}[Al_2(SO_4)_2(OH)_2].$$

Assuming complete dissociation according to the equations:

$$H_2SO_4 = 2H^{\cdot} + SO_4{}''$$
$$Al_2(SO_4)_3 = Al_2(SO_4)_2{}^{\cdot\cdot} + SO_4{}'',$$

and putting x = fractional degree of hydrolysis, we obtain as the equation for the first-stage hydrolysis:

$$\frac{x^3}{(1-x)v^2} = \frac{K_w{}^2}{4k_{b_1}} = K_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12).$$

It might be possible to write the dissociation equilibria, also, as follows:

$$Al_2(SO_4)_3 \rightleftarrows 2AlSO_4{}^{\cdot} + SO_4{}''$$
$$AlSO_4{}^{\cdot} + OH' \rightleftarrows Al(SO_4)(OH),$$

leading thus to the equations:

$$[AlSO_4{}^{\cdot}] \, . \, [OH'] = k_{b_1}[AlSO_4OH]$$
$$[AlSO_4{}^{\cdot}] = \frac{k_{b_1}}{K_w}[AlSO_4OH] \, . \, [H^{\cdot}].$$

In this case, $[AlSO_4{}^{\cdot}] = \frac{2(1-x)}{v}$, $[AlSO_4OH] = \frac{2x}{v}$, $[H^{\cdot}] = \frac{2x}{v}$, and thus the equation corresponding to the first-stage hydrolysis would be

$$\frac{x^2}{(1-x)v} = \frac{K_w}{2k_{b_1}} = K_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13).$$

On this view, the corresponding stoichiometric equation would be:

$$Al_2(SO_4)_3 + 2H_2O = 2Al(SO_4)(OH) + H_2SO_4.$$

Corresponding to the second-stage hydrolysis, we get by similar reasoning the equation :

$$\frac{x^5}{(1-x)v^4} = \frac{K_w^4}{256\,k_{b_2}} = K_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14),$$

where k_{b_2} is the dissociation constant of the basic salt,

$$Al_2(SO_4)(OH)_4,$$

dissociating into the ions $Al_2SO_4^{\cdot\cdot\cdot\cdot}$ and $4OH'$.

In the case of the third-stage hydrolysis, it is possible to write the stoichiometric equation :

$$Al_2(SO_4)_3 + 6H_2O = 2Al(OH)_3 + 3H_2SO_4.$$

The hydrolysis in this case may be supposed to be controlled by the dissociation equilibrium,

$$[Al^{\cdot\cdot\cdot}][OH']^3 = k_{b_3}[Al(OH)_3].$$

Assuming a complete dissociation of $Al_2(SO_4)_3$ according to the equation :

$$Al_2(SO_4)_3 = 2Al^{\cdot\cdot\cdot} + 3SO_4'',$$

we arrive at the equation :

$$\frac{x^4}{(1-x)v^3} = \frac{K_w^3}{6^3 k_{b_3}} = K_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15),$$

where x is the fractional degree of hydrolysis according to the above equation.

In the case of a sulphate of a bivalent cation, there is only one stage of hydrolysis possible, and to this corresponds a cubic equation in x of the same form as equation (10) or (12). Similarly, for the sulphate of a univalent cation, the equation of hydrolytic dissociation is the same as (8).

In attempting to test any of the equations given in the preceding paragraphs, three points must be borne in mind. In the first place, certain simplifying assumptions have been made with respect to the nature and degree of the ionisation of the salts and acids involved. In the second place, the stages of the progressive hydrolysis considered may not be sharply marked off, with the result that a superposition of the different equilibria may occur. Finally, the solubilities of the basic salts or hydroxides may be overstepped, so that heterogeneous equilibria are produced. Furthermore, if, as very often happens, the basic salts or hydroxides separate in the form of colloidal pseudo-solutions or suspensions, it may be expected that no definite equilibria will be obtained.

The second and third of these difficulties reside in the nature of the phenomena themselves, and cannot be surmounted. The first difficulty mentioned may, however, be obviated to a certain extent by introducing suitable corrections. Thus in the preceding theory the total concentration of the acid that must be produced according to the stoichiometric mass-relationship has been identified with the concentration of the hydrogen ion. This will, however, not in general be true, even for the highly dissociated mineral acids. In the case of the chlorides of chromium and aluminium dealt with below, a correction has been made for the undissociated hydrochloric acid on the assumption that the percentage amount of undissociated acid would be the same as in a pure hydrochloric acid solution of the same total concentration of chlorine ions. In the case of the sulphate of aluminium, it has not been possible to apply a similar correction, owing to the want of sufficiently secure data concerning the dissociation of the ion HSO_4'.

Apparatus and Method of Measurement.

The hydrogen electrode employed was constructed after the type described by Wilsmore (*Zeitsch. physikal. Chem.*, 1900, **35**, 296). The other half-element consisted of a normal mercurous chloride electrode. The hydrogen and mercurous chloride electrodes were connected by a saturated solution of ammonium nitrate, which Abegg and Cumming (*Zeitsch. Elektrochem.*, 1907, **13**, 17) have recently shown to annul the liquid potential difference. The rest of the apparatus consisted of a slide-wire bridge, accumulator, cadmium cell, and Lippmann electrometer. The temperature at which the experiments were carried out was 25°, constancy of temperature being secured by a suitable water-thermostat. The hydrogen used for saturating the electrode was prepared from electrolytic zinc and pure dilute sulphuric acid, and passed through a washbottle containing an alkaline solution of potassium permanganate.

The solutions were always prepared from conductivity water ($1{\cdot}2 \times 10^{-6}$ to $2{\cdot}5 \times 10^{-6}$) by siphoning the required quantity on to a weighed amount of the salt. The solutions were kept in steamed-out Jena flasks, and whenever they were kept for more than a day they were protected with a soda-lime tube to guard against the entry of carbon dioxide.

The potential of the hydrogen electrode is given by the formula:

$$\pi_1 - \pi_0 = \frac{RT}{F}\log_e[H^{\cdot}],$$

where π_1 = the potential of a solution of concentration $[H^{\cdot}]$; π_0 = potential for a solution normal in respect to $H^{\cdot}$-ion, and R, T, F have their usual significations. In accordance with the agreement of the Commission on Electrode Potentials of the German Bunsen Society, under electrode potential is here understood positive potential of the electrode—positive potential of solution. If we take the absolute potential of the normal calomel electrode as +0·56 volt, we may (Wilsmore, *loc. cit.*) put $\pi_0 = +0{\cdot}277$ volt. The method of calculation employed may, for the sake of clearness, be briefly illustrated by two examples:

(*a*) Table I, p. 48.

Cell measured, $H_2 \mid n/32C_6H_5\overrightarrow{\cdot NH_3Cl \mid NH_4}NO_3 \mid Hg_2Cl_2$ electrode.

Observed *E.M.F.* = 0·4655 volt (in direction indicated by the arrow). Hence potential of the hydrogen electrode = 0·56—0·4655 = 0·0945 volt, and therefore $\frac{RT}{F}\log_e[H^{\cdot}] = 0{\cdot}0945 - 0{\cdot}277 = -0{\cdot}1825$. As $T = 273 + 25 = 298$, we have $\frac{RT}{F} \times 2{\cdot}3026 = 0{\cdot}059$, and therefore $\log[H^{\cdot}] = -\frac{0{\cdot}1825}{0{\cdot}059}$, whence $[H^{\cdot}] = 0{\cdot}000807$. Since complete hydrolysis would produce a value of $[H^{\cdot}]$ equal to 1/32 (assuming complete dissociation of the hydrochloric acid), the percentage hydrolysis is given by the equation $100x = 0{\cdot}000807 \times 32 \times 100$, whence $100x = 2{\cdot}58$ (x = fractional hydrolysis).

(*b*) Table (XII), p. 57.

Cell measured, $H_2 \mid n/4\overrightarrow{Al_2(SO_4)_3 \mid NH_4NO_3} \mid Hg_2Cl_2$ electrode.

Observed *E.M.F.* = 0·4354 volt.

Potential of H_2-electrode = 0·56—0·4354 = 0·1246 volt.

Hence $0{\cdot}059 \log[H^{\cdot}] = 0{\cdot}1246 - 0{\cdot}277 = -0{\cdot}1524$, whence $[H^{\cdot}] = 0{\cdot}00261$.

Since the solution is one-fourth molecular normal with respect to aluminium sulphate, complete hydrolysis according to the stoichiometric equation:

$$Al_2(SO_4)_3 + 2H_2O = Al_2(SO_4)_2(OH)_2 + H_2SO_4,$$

would yield a one-fourth molecular normal solution of sulphuric acid. If one assumes complete dissociation of the sulphuric acid into the ions $H^{\cdot}$ and SO_4'', the molar concentration of the hydrogen ion would be 0·5. Hence the percentage hydrolysis according to the above reaction is given by the equation:

$$100x = \frac{0{\cdot}00261}{0{\cdot}5} \times 100 = 0{\cdot}52.$$

Aniline Hydrochloride.

The hydrolysis of this salt has been very carefully determined by Bredig (*Zeitsch. physikal. Chem.*, 1894, **13**, 289) and by Walker and

Aston (Trans., 1895, **67**, 576). Bredig used the conductivity method, and found 2·61 per cent. hydrolysed for v_{32} at 25°. Walker used the inversion method, and found 4·5 per cent. for v_{30} at 60°. A redetermination of the hydrolysis of this salt appeared to be a useful test of the method employed in this paper.

The salt used was purified by recrystallisation from a saturated solution in acetone, the solvent being removed by repeated washing with ether. It was finally dried over potassium hydroxide and concentrated sulphuric acid in a vacuum desiccator.

In the table below, as well as in all following tables, v denotes the molecular dilution, *E.M.F.* the measured electromotive force of the cell in volts, π_1 the absolute potential of the hydrogen electrode for that solution, [H˙] is the hydrogen-ion concentration in gram-mols. per litre, and $100x$ is the percentage hydrolysis calculated for a first-stage hydrolysis, unless the contrary is stated.

TABLE I.

Aniline Hydrochloride.

Cell, $H_2 \mid C_6H_5{\cdot}\overrightarrow{NH_3Cl \mid NH_4}NO_3 \mid Hg_2Cl_2$ electrode.

v.	*E.M.F.*	π_1.	$H^{\cdot} \times 10^2$.	$100x$.	$K_1 \times 10^4$.
16	0·4567	0·1033	0·1138	1·82	0·21
24	0·4609	0·0991	0·0966	2·32	0·23
32	0·4655	0·0945	0·0807	2·58	0·21
				Mean…………	0·216

Under K_1 are tabulated the values of the constant calculated from equation (8), $\frac{x^2}{(1-x)v} = K_1$, as deduced for a first-stage hydrolysis of a salt of this type. The hydrolysis for v_{32} amounts to 2·58 per cent., a value agreeing extremely well with that found by Bredig at the same temperature and dilution, 2·61 per cent.

The Apparent Heat of Dissociation of "Anilinium Hydroxide."

The hydrolytic constant of aniline hydrochloride is calculated from equation (8), $\frac{x^2}{(1-x)v} = \frac{K_w}{K_b}$. If the dissociation of a normal electrolyte is measured over a range of temperature not too great, it is generally found to be practically independent of the temperature. Therefore, knowing K_b at 25° and the variation of K_w with the temperature, one should be able to calculate x for any other temperature. But as K_w at 60° is nine times as great as at 25°, it follows that the hydrolysis of aniline hydrochloride for v_{30} at 60° would be 7·5 per cent., whilst

Walker and Aston (*loc. cit.*) found only 4·5 per cent. The conclusion must be drawn that the dissociation constant of "anilinium hydroxide" is not independent of the temperature. An application of van't Hoff's equation,

$$\frac{d \log K_b}{dt} = \frac{RT^2}{q},$$

should therefore give information regarding q, the apparent heat of dissociation. On integrating between the limits T_1, T_2, we get

$$\frac{\log K_b}{K_b'} = \frac{q}{R}\left(\frac{T'' - T'}{T' T''}\right),$$

where K_b'', K_b' are the dissociation constants of "anilinium hydroxide" at the temperatures T'' and T'.

If $\frac{K_w}{K_b}$ is calculated from the percentage hydrolysis obtained by Walker and Aston at 60°, the value $\frac{K_w}{K_b} = 0·707 \times 10^{-4}$ results; at 25°, $\frac{K_w}{K_b} = 0·216 \times 10^{-4}$, and from these results q is calculated to be 2860 calories; q here refers to the heat absorbed in the dissociation of "anilinium hydroxide" *plus* the heat absorbed in the hydration of the anhydrous aniline.

Ammonium Chloride.

The hydrolysis of this salt was recently measured by Veley (Trans., 1905, **87**, 26). The method he used was to boil the solution for an hour, and then determine the loss of ammonia by titration. The conclusion was drawn that the hydrolysis of ammonium chloride must be very small indeed.

As usual, the salt was freed from any traces of acid by repeated recrystallisation from conductivity water. A normal solution was first used, and the potential registered by the hydrogen electrode amounted to $-0·0049$ volt after thirty minutes, but in an hour it had risen to 0·0066 volt. This steady increase in potential, and therefore in hydrogen-ion concentration, pointed to the loss of ammonia, and this was conclusively proved by passing the escaping gas into a solution of red litmus. It very quickly turned a decided blue. In order to overcome this loss of ammonia, three washbottles were inserted before the hydrogen electrode, all containing a solution of the same strength as was being measured. One washbottle was outside the thermostat, and two within. Thus when the hydrogen reached the solution containing the electrode, it was already in equilibrium with ammonia at that temperature and concentration.

One other difficulty still remained. The observed potential was found to fall to a minimum, and then rise a little to a fixed, but higher, value. The steady fall to a minimum is due to the gradual saturation of the electrode with hydrogen, and the subsequent rise can only be due either to the electrode having been supersaturated or to an increase in the hydrogen-ion concentration. The first possibility may be left out of consideration, for in no other salt used did this occur. The increase in the hydrogen-ion concentration can be readily explained as being due to the adsorption of ammonia by the electrode from the film of liquid in contact with it. The potential registered would be that of the surrounding film, and would consequently be too high. The hydrogen and ammonia gases are occluded by the platinum, the former probably with a much greater velocity, and hence the lowest potential registered would, on this assumption, correspond very nearly to the true potential. Slight evidence in support of this is furnished by the fact that the hydrogen-ion concentrations calculated from the higher potentials are practically the same, although the concentration of the solution has changed from $N/2$ to $N/32$; but the hydrogen-ion concentrations calculated from the lower potentials show differences much more in accord with the behaviour of all known hydrolysed salts, that is, with increasing concentration of the salt there is an increasing hydrogen-ion concentration, but a decreasing percentage hydrolysis. As it was a matter of very great difficulty to obtain values for the minimum potential when it changes so quickly, a number of independent experiments were carried out, and the mean minimum potential recorded.

TABLE II.

Ammonium Chloride.

Cell, $H_2 \mid \overrightarrow{NH_4Cl \mid NH_4NO_3} \mid Hg_2Cl_2$ electrode.

v.	*E.M.F.*	π_1.	$[H^{\cdot}] \times 10^6$.	$100x$.	$K_1 \times 10^9$.
2	0·5732	−0·0132	1·233	0·00246	0·30
8	0·5911	−0·0311	0·604	0·00479	0·29
16	0·5998	−0·0398	0·427	0·0068	0·29
32	0·6056	−0·0456	0·340	0·0108	0·36
				Mean............	0·31

The constant K_1 is calculated from equation (8), $\frac{x^2}{(1-x)}v = K_1$, for a first-stage hydrolysis of a salt with univalent anion. The experimental error arising from the adsorption mentioned has prevented more dilute solutions being examined, but enough has been done to show how small is the hydrolysis of this salt.

The ratio for the hydrolytic constants of aniline hydrochloride and ammonium chloride is seventy thousand, that is, aniline is seventy thousand times as weak a base as ammonium. Bredig (*Zeitsch. physikal. Chem.*, 1895, **13**, 289) has found the dissociation-constant of ammonium hydroxide to be 0·0023, and Abegg (*Die elekt. Dissociation-theorie*, Ahrens' "Vorträge," **8**, 183) gives the dissociation-constant of aniline as $4{\cdot}9 \times 10^{-10}$. The ratio of the constant of ammonia to that of "anilinium hydroxide" is 50,000. Since the hydrolytic constant of aniline hydrochloride agrees so well with that found by Bredig, we are justified in concluding that the hydrolytic constant of ammonium chloride is tolerably correct.

Moreover, Noyes, in his report, "The Electrical Conductivity of Aqueous Solutions" (p. 346), has calculated the per cent. hydrolysis of ammonium chloride ($v = 100$) to be 0·02 at 18°, whilst extrapolation from the above values (Table II) gives 0·018 for this dilution at 25°.

Chromium Chloride.

A great deal of work has been done on the green and blue modifications of chromium chloride. Amongst others, the work of Godefroy (*Compt. rend.*, 1885, **100**, 105); Peligot (*Compt. rend.*, 1885, **100**, 105); Recoura (*Ann. Chim. Phys.*, 1887, [vi], **10**, 39); Werner and Gubser (*Ber.*, 1901, **34**, 1579), and Gubser (*Inaug. Diss.*, Zurich, 1900) may be mentioned. The work of these goes to show that the formula of both varieties is $CrCl_3,6H_2O$, but in the green chloride two atoms of chlorine cannot be precipitated by silver nitrate, as they form part of a complex cation. Recently, Bjerrum (*Zeitsch. physikal. Chem.*, 1907, **59**, 336) has shown that the blue chloride, when dissolved in water, is hydrolysed, thus:

$$CrCl_3 + H_2O = CrCl_2(OH) + HCl.$$

The hydrolytic constant of the green salt is only about one four-hundredth that of the blue. The method used by him to measure the hydrolysis was the determination of the potential of the hydrogen electrode and conductivity measurements.

Hydrolysis of the Green Chloride.—This chloride was prepared according to the method described by Recoura (*loc. cit.*) and Werner and Gubser (*loc. cit.*).

Bjerrum has very carefully examined the solution of the green chloride, using an apparatus whereby he was enabled to obtain a potential within two minutes, and a conductivity measurement in even less time. He has found that the hydrolysis as indicated by the potential observed is at first much less than for the blue chloride, but that there is a rapid increase of hydrolysis in the first few hours. Unfortunately, the apparatus used in the present work was unsuitable for obtaining readings in such a short time, for it required at least ten minutes to obtain a constant potential. A more or less qualitative series of experiments with the green solution has therefore been carried out in order to check Bjerrum's results.

A solution of the green chloride was prepared and divided into two parts, and to one was added a few drops of concentrated hydrochloric acid. These two samples were allowed to stand at the ordinary temperature. In sixteen hours, that which had not been acidified was bluish-green, whilst the other remained green. In three days, the latter was still unchanged, but the unacidified sample was blue. The addition of the acid had evidently retarded the formation of the blue salt from the green, consequently the change of the green into the blue must be attended by the increase of acid concentration through an increase of hydrolysis.

A solution of concentration v_{64} was then prepared, and readings were taken for two hours; t denotes the time in minutes since the solution was made.

Table III.

Cell, $H_2 \mid CrCl_3$ (green) $\overrightarrow{\mid NH_4NO_3 \mid}$ Hg_2Cl_2 electrode.

$v = 64.$

t.	*E.M.F.*	π_1.	$[H^\cdot] \times 10^2$.
20	0·4545	0·1055	0·124
40	0·4526	0·1074	0·133
120	0·4458	0·1142	0·174

Table IV.

$v = 16.$

t.	*E.M.F.*	π_1.	$[H^\cdot] \times 10^2$.
20	0·4355	0·1245	0·260
35	0·4268	0·1332	0·317
45	0·4220	0·1380	0·441
75	0·4180	0·1420	0·514
105	0·4180	0·1420	0·514

Table V.

$v = 32.$

t.	*E.M.F.*	π_1.	$[H^\cdot] \times 10^2$.
15	0·4559	0·1041	0·117
32	0·4471	0·1129	0·166
55	0·4368	0·1232	0·247

These experiments all show that there is a rapid rise in the hydrogen-ion concentration, and, as the hydrolytic constant found by Bjerrum and by me for the blue chloride is very much larger than the approximate constant found by him for the green chloride, he is quite justified in his conclusion that the rapid increase in hydrolysis is due to a progressive conversion of the green chloride into the blue.

Chromium Chloride (blue).

The salt was prepared as described by Higley (*J. Amer. Chem. Soc.*, 1904, **26**, 613).

TABLE VI.

Cell, H_2 | $CrCl_3$ | $\overrightarrow{NH_4NO_3}$ | Hg_2Cl_2 electrode.

v.	*E.M.F.*	π_1.	$[H^{\cdot}] \times 10^2$.	Total $[H^{\cdot}] \times 10^2$.	$100x$.
4	0·4234	0·1366	0·417	0·510	2·02
8	0·4332	0·1278	0·296	0·351	2·81
16	0·4382	0·1218	0·234	0·269	4·30
32	0·4455	0·1145	0·176	0·197	6·30
64	0·4523	0·1077	0·135	0·148	9·47

In Table VI, "total $[H^{\cdot}]$" refers to the concentration of the hydrogen ion after a correction has been made for the undissociated hydrochloric acid, as already explained. Figure 1 shows x plotted as a function of v.

TABLE VII.

v.	$100x$.	$K_1 \times 10^3$.	$K_2 \times 10^7$.
4	2·02	0·10	0·65
8	2·81	0·10	0·43
16	4·30	0·12	0·40
32	6·30	0·13	0·31
64	9·47	0·15	0·27
	Mean............	0·12	

Here K_1 refers to the constant calculated for a first-stage hydrolysis from equation (8), $\frac{x^2}{(1-x)v} = K_1$; and K_2 has been calculated for a second-stage reaction according to equation (10), $\frac{x^3}{(1-x)v^2}$, x here being, also, calculated for a second-stage reaction, that is, half the values tabulated above. Although K_1 varies somewhat, its variation is much less than that of K_2. Undoubtedly, therefore, the main reaction must be represented by the ionic equation :

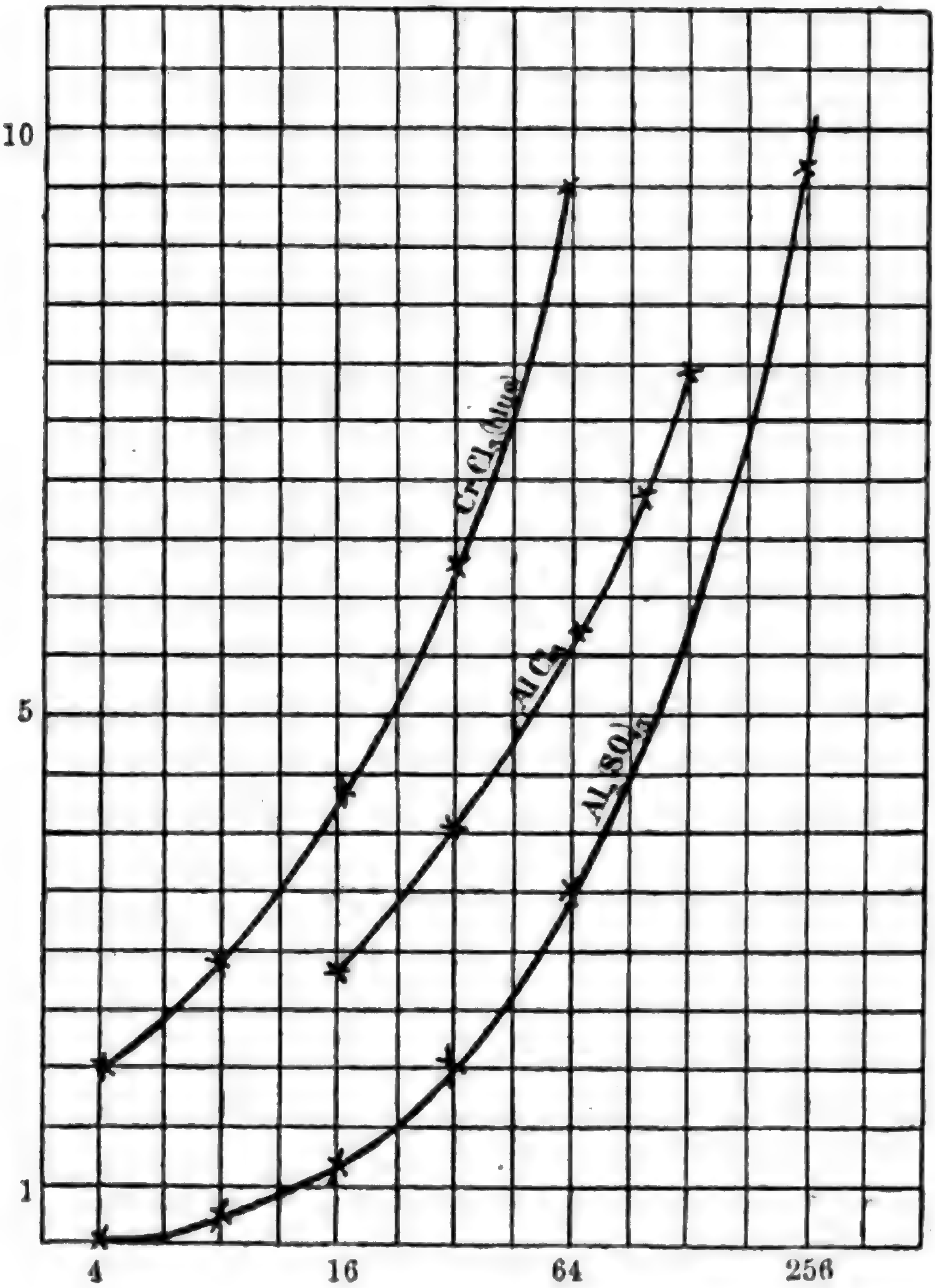
$$CrCl_2^{\cdot} + H_2O \rightleftharpoons CrCl_2(OH) + H^{\cdot},$$

but probably the basic salt, $CrCl(OH)_2$, is also produced in the dilute solutions as in the equation :

$$CrCl^{\cdot\cdot} + 2H_2O \rightleftharpoons CrCl(OH)_2 + 2H^{\cdot}.$$

At any rate, Bjerrum (*loc. cit.*) has also noticed the rise in the constant in the dilute solutions. The percentages of hydrolysis given in Table VI are slightly larger than Bjerrum found, for his constant amounts to $0{\cdot}98 \times 10^{-4}$, as compared with $1{\cdot}2 \times 10^{-4}$, but considering the great influence a slight error in the *E.M.F.* exerts, the agreement must be considered quite satisfactory.

FIG. 1.



Aluminium Chloride.

This salt was prepared from a specimen obtained from Merck by precipitating it from a saturated solution with hydrogen chloride. The salt was left for a month in a vacuum desiccator over potassium hydroxide to remove any traces of adhering acid.

Preliminary experiments with zinc sulphate, which will be described later, had already shown that a solution of this salt does not give the same hydrogen-ion potential from day to day, but that an extraordinary change in the hydrogen-ion concentration of the solution occurs. Thus it was important to determine whether the solution of each salt examined gave a constant potential over a considerable number of days, proving that the solution was in a state of equilibrium. This was done in a "time" experiment, wherein a quantity of a solution was siphoned from the main stock into the apparatus every day, and its potential ascertained for a sufficient number of days to show that equilibrium had set in. It was not necessary to do this in the case of the chromium salts, because it is known from the work of Richard and Bonnet (*loc. cit.*) and Bjerrum that the solutions slowly change their hydrogen-ion concentrations until equilibrium is reached; nor were "time" experiments carried out with aniline hydrochloride or ammonium chloride, for here there is no possibility of solid basic salts or hydrates complicating the ionic reactions.

The "time" experiment for aluminium chloride showed that within twenty-four hours a state of equilibrium is reached, as is shown in the following table.

TABLE VIII.

Cell, $H_2 \mid AlCl_3 \overrightarrow{\mid NH_4NO_3} \mid Hg_2Cl_2$ electrode.

Day.	*E.M.F.*
April 26	0·4485
,, 26	0·4537
,, 27	0·4607
April 27	0·4607
,, 29	0·4605
,, 29	0·4606

All solutions in the following experiments were therefore allowed to stand in the thermostat for twenty-four hours before measurements were made.

TABLE IX.

Aluminium Chloride.

Cell, $H_2 \mid AlCl_3 \overrightarrow{\mid NH_4NO_3} \mid Hg_2Cl_2$ electrode.

v.	*E.M.F.*	π_1.	$[H^{\cdot}] \times 10^2$.	Total $[H^{\cdot}] \times 10^2$.	$100x$.
16	0·4492	0·1108	0·1520	0·1750	2·8
32	0·4567	0·1023	0·1140	0·1270	4·06
64	0·4655	0·0945	0·0807	0·0885	5·66
100	0·4720	0·0880	0·0626	0·0679	6·79
128	0·4741	0·0859	0·0577	0·0620	7·93

Figure 1 shows x plotted as a function of v.

TABLE X.

v.	$100x$.	$K_1 \times 10^4$.
16	2·80	0·50
32	4·06	0·53
64	5·66	0·53
100	6·79	0·49
128	7·93	0·53
	Mean............	0·51

K_1 is calculated from equation (8) for a first-stage hydrolysis, $\frac{x^2}{(1-x)v}=K_1$; the value obtained clearly shows that the hydrolysis proceeds according to the ionic equation:

$$AlCl_2^{\cdot} + H_2O \rightleftharpoons AlCl_2(OH) + H^{\cdot}.$$

A comparison of the percentage hydrolysis of chromium and aluminium chlorides at similar dilutions shows that the chromium chloride is, on the average, hydrolysed 1·6 times as much as the aluminium chloride. From these experiments, it would appear that chromium is about 1·6 times as weak a base as aluminium.

Comparison of Results for Aluminium Chloride.

Kahlenberg, Davis and Fowler (*loc. cit.*) have found 2·2 per cent. hydrolysed in a sixth-molecular normal solution at 55·5°. Ley (*loc. cit.*), working at 99·7°, where the hydrolysis is much greater, obtained the following results.

TABLE XI.

v.	$100x$.	$K_1 \times 10^4$.
32	8·04	2·2
64	13·20	3·1
128	19·70	3·8
256	28·20	4·3
512	41·40	5·7

Here x and K_1 refer to a first-stage hydrolysis, the latter being calculated from equation (8), $\frac{x^2}{(1-x)v}=K_1$.

His results at 99·7° are roughly about twice those observed by the author at a lower temperature.

Ley has made one determination of the hydrolysis of aluminium chloride by conductivity methods at 25°. He found 13·5 per cent. hydrolysed at v_{1024}.

Bruner (*loc. cit.*) worked at 40° and found at v_4 3·3 per cent., at v_8 2·9 per cent., and at v_{32}, 2·9 per cent. hydrolysed. He is the only worker who has not found increasing hydrolysis of this salt on dilution.

Recently, Bjerrum (*loc. cit.*, p. 349) carried out a series of experiments on the hydrolysis of aluminium chloride at 25°, using conductivity measurements. He says "Ley hat früher die Hydrolyse des Aluminiumchlorids in 3/1024-molarer Lösung zu 4·5 pro cent. (alle Salzsäure frei = 100 pro cent.) berechnet. Dieses entspricht 13·5 pro cent. Hydrolyse nach der Gleichung $AlCl_3 + H_2O = AlCl_2OH + HCl$. Ich finde 16·6 pro cent." Two misstatements occur here. Ley worked throughout (*loc. cit.*) with molecular solutions, and it was in a solution 1/1024-*molecular* normal that he obtained 13·5 per cent. hydrolysis; secondly, the solution in which Bjerrum records 16·6 per cent. hydrolysis is, according to his own table, one containing 0·000326 of a gram-molecule, that is, $v = 3069$. These misstatements both appear to be due to confusion between molecular normality and equivalent normality. Further comparison of Bjerrum's results must be left over until the errors mentioned have been corrected.

Aluminium Sulphate.

The salt was obtained from Merck, and was freed from any traces of acid by precipitating it from a saturated solution by the addition of alcohol.

Just as in the case of aluminium chloride, there was a slight change of hydrolysis in the "time" experiment during the first day, but after that time the potential registered remained quite constant for the next three days. In the following experiments, the solutions were kept twenty-four hours in the thermostat before measurements were made.

TABLE XII.

Aluminium Sulphate.

Cell, $\mathrm{H_2} \vdots \mathrm{Al_2(SO_4)_3} \overrightarrow{\mid \mathrm{NH_4NO_3}} \mid \mathrm{Hg_2Cl_2}$ electrode.

v.	*E.M.F.*	π_1.	$[\mathrm{H}^{\cdot}] \times 10^2$.	$100x$.	$K_1 \times 10^8$.	$K \times 10^5$.
4	0·4354	0·1246	0·261	0·522	0·88	0·68
8	0·4439	0·1161	0·187	0·748	0·66	0·71
16	0·4505	0·1095	0·145	1·160	0·62	0·85
32	0·4541	0·1059	0·126	2·016	0·82	1·30
64	0·4585	0·1016	0·106	3·492	0·98	1·86
256	0·4672	0·0928	0·075	9·600	1·48	4·00

Figure (1) shows the variation of x with v. In the above table, K_1 is calculated from equation (12), $\frac{x^3}{(1-x)v_2} = K_1$, for a first-stage hydrolysis of a salt of this type. The rise in the value of K_1 from v_{256}

points to the probability that with increasing dilution the second-stage hydrolysis is becoming increasingly important. The reaction from v_4 to v_{64} is represented by the stoichiometric equation:

$$Al_2(SO_4)_3 + 2H_2O = Al_2(SO_4)_2(OH)_2 + H_2SO_4,$$

and by the ionic equation:

$$Al_2(SO_4)_2^{\cdot\cdot} + 2H_2O \rightleftarrows Al_2(SO_4)_2(OH)_2 + 2H^{\cdot},$$

but in more dilute solutions we have also:

$$Al_2(SO_4)_3 + 4H_2O = Al_2(SO_4)(OH)_4 + 2H_2SO_4$$
$$Al_2(SO_4)^{\cdot\cdot\cdot\cdot} + 4H_2O \rightleftarrows Al_2(SO_4)(OH)_4 + 4H^{\cdot}.$$

The constant K in the above table has been calculated from equation (13), $\frac{x^2}{(1-x)v}$. This equation has been deduced on the assumption that the reaction is represented by the stoichiometric equation:

$$Al_2(SO_4)_3 + 2H_2O = 2Al(SO_4)(OH) + H_2SO_4,$$

and the ionic equation:

$$AlSO_4^{\cdot} + OH' \rightleftarrows Al(SO_4)(OH).$$

The constant K shows considerably more variation than does K_1, although in the concentrated solutions K is as constant as can be expected for such concentrations.

Comparison of Results for Aluminium Sulphate.

Bruner (*loc. cit.*) at 40° found 1·3 per cent. hydrolysed at v_{12}, 1·4 per cent. at v_{20}, and 1·7 per cent. at v_{40}.

Ley (*loc. cit.*) at 99·7° found 8·9 per cent. at v_{256}, and 5·4 per cent. at v_{128}.

Kahlenberg, Davis and Fowler (*loc. cit.*) at 55·5° found a hydrolysis of 1·56 per cent. for v_{12}.

Finally, Carrara and Vespignani (*loc. cit.*) measured the hydrolysis of this salt at 25° by the inversion of methyl acetate. The basis of this method is to compare the constant of the reaction for a salt with that obtained for a dilute solution of an acid where the dissociation is complete, that is, where the hydrogen-ion concentration can be identified with the total-acid concentration. Now these workers have compared their constant for aluminium sulphate with that of sulphuric acid, both fifth-molecular normal, and thus obtained a percentage hydrolysis of 2·6. It is obviously incorrect to identify the hydrogen-ion concentration of a fifth-molar solution of sulphuric acid with that of the total acid, and any such assumption must cause a very large error in the calculation. If the percentage hydrolysis is calculated from the constant of aluminium sulphate and that obtained by them for hydrochloric acid (v_5), according to the equation, percentage $= \frac{100k.v/2}{K_a v_a}$, the result is 0·81. But a fifth-molar solution of hydrogen chloride is only dissociated to the extent of 80 per cent., and on correcting for this the percentage is found to be 0·65. This agrees extremely well with the value 0·52 given in Table XII for v_4.

Thallous Sulphate.

The salt was supplied by Kahlbaum, and was not further purified. The solutions were all acid towards litmus, and owing to the sparing solubility of the sulphate only a few solutions were examined. Although the solution v_{16} was observed for several days, no change in the amount of hydrolysis was detected. Apparently the hydrolytic equilibrium is established immediately on preparing the solution.

TABLE XIII.

Cell, $H_2 \mid Tl_2SO_4 \overrightarrow{\mid NH_4NO_3 \mid} Hg_2Cl_2$ electrode.

v.	*E.M.F.*	π_1.	$[H^\cdot] \times 10^2$.	$100x$.	$K_1 \times 10^3$.
16	0·4137	0·1463	0·609	4·87	0·15
32	0·4213	0·1387	0·448	7·15	0·17
64	0·4309	0·1291	0·311	9·95	0·17
				Mean............	0·16

The constant K_1 is calculated from equation (8), $\frac{x_2}{(1-x)v}$, for a first-stage hydrolysis of a salt with univalent cation; the value of K_1 is practically constant, and this shows that the hydrolysis must proceed according to the ionic equation:

$$Tl^\cdot + OH' \rightleftarrows Tl(OH).$$

Nickel Sulphate.

The salt was prepared from a specimen of Kahlbaum's by careful recrystallisation. The "time" experiment again showed a variation in the hydrogen-ion concentration, although much less than observed in the salts of zinc, magnesium, thorium, and cerium.

TABLE XIV.

Nickel Sulphate; $v = 32$.

Cell, $H_2 \mid NiSO_4 \mid \overrightarrow{NH_4NO_3} \mid Hg_2Cl_2$ electrode.

Days.	*E.M.F.*	π_1.	$[H^\cdot] \times 10^3$.
0	0·5031	0·0569	0·186
1	0·4966	0·0634	0·230
3	0·4962	0·0638	0·244
4	0·5023	0·0577	0·192
5	0·5003	0·0597	0·207
6	0·4998	0·0602	0·211

The first column denotes the age of the solution in days.

In the following series of experiments, in order to make the results comparable, the potentials were measured ten minutes after the solutions were made; but as the "time" experiment shows a slight variation in the hydrogen-ion concentration, one cannot expect to obtain a satisfactory constant.

TABLE XV.

Cell, $H_2 \mid NiSO_4 \mid \overrightarrow{NH_4NO_3} \mid Hg_2Cl_2$ electrode.

v.	*E.M.F.*	π_1.	$[H^\cdot] \times 10^4$.	$100x$.	$K_1 \times 10^{12}$.	$K \times 10^8$.
4	0·5302	0·0298	0·647	0·013	0·14	0·42
8	0·5362	0·0238	0·512	0·020	0·13	0·52
16	0·5400	0·0200	0·440	0·035	0·17	0·77
32	0·5518	0·0082	0·278	0·044	0·09	0·62
64	0·5637	−0·0037	0·175	0·056	0·04	0·49
				Mean............	0·11	

K_1 has been calculated from equation (12), $\frac{x^3}{(1-x)v^2} = K_1$, for a first-stage hydrolysis of a salt of this type; K is the constant calculated from equation (13), $\frac{x^2}{(1-x)v} = K$.

The first constant K_1 is sufficiently satisfactory to show that the hydrolysis proceeds according to the ionic equation:

$$Ni^{\cdot\cdot} + 2OH' \rightleftarrows Ni(OH)_2.$$

The constant K is again satisfactory, although the equation from which it is calculated lacks the possible theoretical foundation that it has in the case of aluminium and chromium sulphates.

Kahlenburg, Davis and Fowler (*loc. cit.*) have measured the hydrolysis of nickel sulphate (v_4) at 55·5°, and found 0·045 per cent. hydrolysed. This compares well with that quoted in the above table for the same dilution, namely, 0·013 per cent. at 25°.

Cobalt Sulphate.

This salt was prepared from a specimen of cobalt carbonate (free from nickel) by the action of sulphuric acid. The sulphate so formed was three times precipitated from a strong solution by the addition of alcohol. Finally, the sulphate was recrystallised from water. The "time" experiment was followed for five days, but the hydrogen-ion concentration showed very little change from the value first obtained.

TABLE XVI.

Cell, $H_2 \mid CoSO_4 \overrightarrow{\mid NH_4NO_3 \mid} Hg_2Cl_2$ electrode.

v.	$E.M.F.$	π_1.	$[H^{\cdot}] \times 10^4$.	$100x$.	$K_1 \times 10^{14}$.	$K \times 10^9$.
2	0·5487	0·0113	0·313	0·0031	0·76	0·48
4	0·5590	0·0010	0·210	0·0042	0·46	0·44
8	0·5675	− 0·0075	0·163	0·0065	0·43	0·53
16	0·5762	− 0·0162	0·107	0·0085	0·24	0·45
32	0·5798	− 0·0198	0·093	0·0149	0·32	0·69
				Mean............	0·44	

In table XVI, K_1 is calculated from equation (12), $\frac{x^3}{(1-x)v^2} = K_1$, for a first-stage hydrolysis of such a salt. The value of K_1 is much too high in the strongest solution, but for the others it is sufficiently satisfactory to show that the ionic reaction is:

$$Co^{\cdot\cdot} + 2OH' \rightleftharpoons Co(OH)_2.$$

Here, also, K, calculated from the equation (13), $\frac{x^2}{(1-x)v} = K$, gives a much better constant, and yet this equation again appears to lack a theoretical basis.

Nickel Chloride.

The salt was purified by careful recrystallisation. A solution of medium strength was measured for four days, and a decided increase of the hydrogen-ion concentration took place within the first twenty-four hours, rising from 0·00014 to 0·00018. No change beyond the limits of error occurred on the three succeeding days. In the following experiments, all solutions were therefore allowed to stand in the thermostat for twenty-four hours before being measured.

In order to obtain the hydrolytic constant, a concentrated solution was prepared and its strength determined by analysis; other solutions were prepared from this by dilution.

TABLE XVII.

Cell, $H_2 \mid NiCl_2 \overrightarrow{\mid NH_4NO_3 \mid} Hg_2Cl_2$ electrode.

v.	*E.M.F.*	π_1.	$[H^{\cdot}] \times 10^3$.	$100x$.	$K_1 \times 10^6$.
4·4	0·4927	0·0683	0·290	0·127	0·36
8·8	0·5032	0·0568	0·184	0·16	0·29
17·6	0·5109	0·0481	0·132	0·23	0·27
35·2	0·5229	0·0371	0·086	0·30	0·30
				Mean............	0·30

The values under K_1 are calculated from equation (8), $\frac{x^2}{(1-x)v}$, for a first-stage hydrolysis of a salt with a univalent anion. The satisfactory nature of the constant shows that the reaction is correctly represented by the ionic equation :

$$NiCl^{\cdot} + OH' \rightleftarrows NiCl(OH).$$

Zinc Sulphate.

The salt was purified by recrystallising it three times from conductivity water; an analysis gave $SO_4 = 33·43$ and 33·41, whilst theory requires $SO_4 = 33·40$ per cent.

The "time" experiment for this salt was, as usual, carried out with every precaution against chance impurities; but, although various solutions were measured daily for four weeks, yet no sign appeared of an equilibrium having been reached, the hydrogen-ion concentration varying irregularly from day to day.

A solution of zinc chloride showed an exactly similar phenomenon.

Owing to the similarity between zinc and magnesium sulphates, it was expected that a similar variation in the hydrogen-ion concentration, that is, in the hydrolysis, would be met with. The variation was again observed, but not to so marked an extent as in zinc sulphate. The percentage calculated for magnesium sulphate of concentration v_{32} from the mean hydrogen-ion concentration is 0·0023, agreeing well with that found by Carrara and Vespignani. They used a fifth-molecular normal solution, and found 0·0047 per cent. at the same temperature.

Thorium sulphate ($v = 64$) has also been examined. The "time" experiment again showed that the hydrolysis is by no means a constant quantity. The variations were not large, but yet quite measurable. The mean percentage for v_{64} is 46.

Solutions of cerium chloride showed undoubted variations in the hydrolysis from day to day. The mean percentage for v_{64} is 0·14, whilst Ley found 0·5 for the same dilution at 99·7°.

Finally, it may be mentioned that cobalt chloride shows considerable variation in solution; the mean percentage for v_{32} is 0·17, and for v_{16} 0·11.

The most probable explanation of the peculiar behaviour of these salts lies in the theory that the hydrolysis leads to a heterogeneous system, and that basic salts and hydrates are present in colloidal suspension.

Summary.

1. The preceding experiments have proved that the hydrogen electrode can be used to determine the hydrolysis of salt solutions even when the hydrogen-ion concentration is as low as $0·3 \times 10^{-6}$ (see ammonium chloride).
2. The hydrolytic constant of ammonium chloride proves ammonia to be about 70,000 times as strong a base as aniline.
3. The salts of chromium are hydrolysed about 1·6 times as much as the salts of aluminium, and chromium may therefore be considered about 1·6 times as weak a base as aluminium.
4. Nickel salts are more strongly hydrolysed than those of cobalt, and in this connexion it is significant that the electropotential of cobalt is higher than that of nickel (Wilsmore, *loc. cit.*).
5. The salts of zinc, magnesium, cerium, thorium, cobalt, and, to a slight degree, nickel show peculiar behaviour in so far as their solutions present a variable degree of hydrolysis from day to day.

In conclusion, I wish to acknowledge my deep debt of gratitude to Professor F. G. Donnan for his ever-ready assistance and kindly encouragement during the course of these experiments.

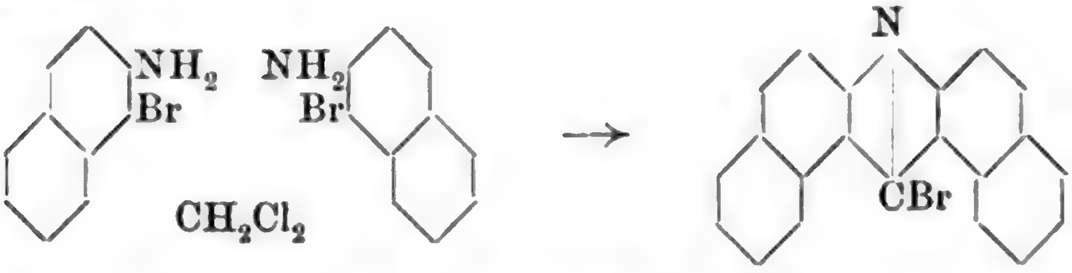
THE MUSPRATT LABORATORY OF
PHYSICAL AND ELECTRO-CHEMISTRY,
UNIVERSITY OF LIVERPOOL.

VI.—*Attempted Synthesis of* $\begin{array}{c}\beta\text{-N-}\beta\\ |\\ \beta\text{-CH}\beta\end{array}$*-Dinaphthacridines: Condensation of Methylene Dichloride and 1-Substituted-2-naphthylamines.*

By ALFRED SENIER and PERCY CORLETT AUSTIN.

Two of the six theoretically possible dinaphthacridines (Senier and Austin, Trans., 1906, **89**, 1387) are still unknown, and our attempts to synthesise derivatives of one of these by using *β*-naphthylamines in which the neighbouring α-position is substituted have led only to the formation of dinaphthacridines of the $\begin{smallmatrix}\beta\text{-N-}\beta\\ |\\ \alpha\text{-CH}\alpha\end{smallmatrix}$ type. But, although we have not succeeded in obtaining the desired compounds, the results in themselves possess sufficient interest to be recorded.

In view of the experiments described in a former paper on halogen addition compounds (Senier and Austin, Trans., 1904, **85**, 1196) and of recent work by A. E. Dunstan and Hilditch (Trans., 1907, **91**, 1659) on the substitution of halogens in acridines by working with hot solutions, the bromo-substitution derivative of $\begin{smallmatrix}\beta\text{-N-}\beta\\ |\\ \alpha\text{-CH}\alpha\end{smallmatrix}$-dinaphthacridine described is worthy of note. It undoubtedly contains the halogen in the meso-carbon position, for the linking of the naphthylene groups by means of the meso-carbon must take place at the position previously occupied by the bromine. Further, it is important to observe that this synthesis effectually removes any doubt that remained as to the constitution of Reed's dinaphthacridine, the proof of which until now was incomplete, since it depended in part on the assumption of Strohbach (*Ber.*, 1901, **34**, 4146) that the α-position in β-naphthylamine is more readily substituted than the other β-position:



Taking into consideration the general fact that a linear arrangement of the rings in the synthesis of cyclic compounds is only obtained with difficulty (Senier and Austin, *loc. cit.*), it was expected that it would not be easy to prepare the $\begin{smallmatrix}\beta\text{-N-}\beta\\ |\\ \beta\text{-CH}\beta\end{smallmatrix}$ base, for this contains a linear arrangement of rings on either side of the acridine nucleus, the only known dinaphthacridine containing a linear arrangement, and that only on one side, being Strohbach's $\begin{smallmatrix}\beta\text{-N-}\beta\\ |\\ \alpha\text{-CH}\beta\end{smallmatrix}$ isomeride. Again, in view of the fact that when β-naphthylamine condenses with methylene dihalides or with formaldehyde the neighbouring α-position enters into the reaction, it was hoped that by fixing the α-position before the experiment by substitution the condensation might then affect the other β-position and give the type of acridine desired. Methylene dichloride was selected as a condensing reagent, because, unlike formaldehyde, it reacts with both β- and α-naphthylamines and because the behaviour of formaldehyde with 1-substituted-2-naphthylamines has already been the subject of an investigation by Morgan (Trans., 1900, **77**, 814), in which no indication of the condensation we wished to bring about was observed.

The results of our experiments show that when the α-position next to that occupied by the amino-group in β-naphthylamine is taken by an easily replaceable element, such as chlorine or bromine, such substituents are eliminated and condensation takes place at the α-position with the formation either of Reed's base or, in the case of bromine, of a bromo-derivative of that base; but that when the α-position is taken by such a substituent as the nitro-group, which is not easily replaced, no condensation takes place.

1. *Interaction of Methylene Dichloride and* 1-*Chloro*-2-*naphthylamine.*

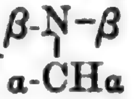
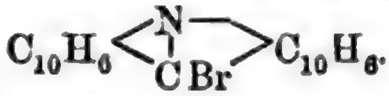
Five grams of 1-chloro-2-naphthylamine were heated in a closed tube with 2½ c.c. (excess) of methylene dichloride for a short time to 200°, when an orange sublimate was noticed at the end of the tube. After the first appearance of this sublimate, the heating was only continued for about fifteen minutes. More prolonged heating or higher temperatures led to unsatisfactory results. When the tube was opened, the contents were first washed with a little cold acetone, then boiled with methylated spirit to which a little aqueous ammonium hydroxide was added, and poured into cold water. After decanting the liquid and recrystallising the dried residue from benzene, large triboluminescent crystals containing no halogen and melting at 216° were obtained. They were identified with

$\begin{matrix}\beta\text{-N-}\beta\\ | \\ \alpha\text{-CH}\alpha\end{matrix}$-dinaphthacridine (Reed).

2. *Preparation of* 1-*Bromo*-2-*naphthylamine.*

In preparing 1-bromo-2-naphthylamine by the method given by Morgan (*loc. cit.*), it was found to be of advantage to warm the solution of aceto-β-naphthalide in glacial acetic acid to about 60° and to add more of the solvent whenever the mass became too thick to stir, otherwise an intimate mixture of the reagents was not obtained. Moreover, the brown precipitate thus formed was purified before hydrolysis. This was done by boiling it with methylated spirit until no more dissolved, and filtering, when it was found that the alcoholic filtrate contained bromoacetonaphthalide in a fairly pure condition. This solution was then hydrolysed by boiling with hydrochloric acid, and the hydrochloride thus obtained was treated with alkali to liberate the base. One crystallisation from light petroleum was generally sufficient to yield crystals of pure 1-bromo-2-naphthylamine.

3. *Interaction of Methylene Dichloride and* 1-*Bromo*-2-*naphthylamine.*

7-Bromo-$\begin{array}{c}\beta\text{-N-}\beta\\ |\\ \alpha\text{-CH}\alpha\end{array}$*-dinaphthacridine,* $C_{10}H_6\!<\!\begin{array}{c}N\\ |\\ CBr\end{array}\!>\!C_{10}H_6.$

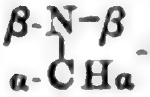
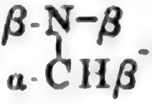
After several partially successful attempts to determine the proper conditions, we found that a temperature of 230—240° was most suitable for bringing about the acridine condensation. In our first experiment, we heated the closed tube to 200° and obtained as the chief product a black, non-crystallisable substance, insoluble in benzene, but soluble in alcohol. Distillation of this black substance under reduced pressure gave rise to a yellow substance, which could not be crystallised and was not further examined. The latter compound is possibly dinaphthacridone.

Satisfactory results were, however, obtained by heating 5 grams of 1-bromo-2-naphthylamine with 2 c.c. of methylene dichloride in a closed tube to 230—240° for three-quarters of an hour. It was not found advisable to work with larger quantities. The contents of the opened tube were easily removed by boiling with methylated spirit containing some potassium hydroxide in solution.

A heavy, black, oily substance was obtained, which, when washed by decantation with cold water, solidified. This was rubbed with a little cold acetone, drained on a filter, and dried in a desiccator. It was then boiled with benzene, and the highly fluorescent, but dark, solution filtered from an insoluble residue, mixed with animal charcoal, boiled for two hours under a reflux condenser, and again filtered and allowed to stand. The solution was thereby rendered much clearer, and slowly deposited well-formed, pale brown crystals. One or two further recrystallisations from benzene sufficed to purify them. When pure they are of a very pale yellow colour and melt at 215·5° (corr.) They contain bromine, but are not triboluminescent. On analysis:

0·1564 gave 0·4011 CO_2 and 0·0500 H_2O. $C = 69·94$; $H = 3·54$.
0·1920 „ 6·7 c.c. nitrogen at 14° and 756 mm. $N = 4·08$.
0·0853 „ 0·0452 AgBr. $Br = 22·54$.

$C_{21}H_{12}NBr$ requires $C = 70·39$; $H = 3·35$; $N = 3·91$; $Br = 22·34$ per cent. The substance is evidently a *monobromodinaphthacridine*. It is essentially different from a dinaphthacridine bromide (compare Senier and Austin, Trans., 1904, **85**, 1196), since it may be boiled with alcoholic potassium hydroxide and may even be distilled in a partial vacuum without decomposition.

According to the method of formation, it might be a derivative either of Reed's or of Strohbach's base, that is, either 7-bromo-$\begin{array}{c}\beta\text{-N-}\beta\\ |\\ \alpha\text{-CH}\alpha\end{array}$-dinaphthacridine or 1-bromo-$\begin{array}{c}\beta\text{-N-}\beta\\ |\\ \alpha\text{-CH}\beta\end{array}$-dinaphthacridine.

It is readily soluble in chloroform or carbon disulphide, less so in benzene or toluene, and very sparingly so in alcohol. It dissolves easily in hot glacial acetic acid, depositing yellow crystals on cooling. The latter melt at 273° and have not yet been investigated. The *hydrochloride* of the base is yellow, and is precipitated from an alcoholic solution by means of hydrochloric acid. No method was found for purifying it. The preparation of double salts with metals was difficult, owing to the fact that no very suitable solvent could be found.

The *aurichloride*, $[C_{21}H_{12}NBr]_3,[HAuCl_4]_2$, was obtained as a yellow, flocculent precipitate when a few drops of auric chloride solution were added to a solution of the base in a mixture of alcohol and acetic acid. The yellow precipitate was washed with dry ether and dried at 105°. On analysis:

0·0694 gave 0·0156 Au. Au = 22·47.

$C_{63}H_{38}N_3Cl_8Br_3Au_2$ requires Au = 22·46 per cent.

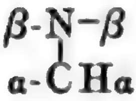
The *platinichloride*, $[C_{21}H_{12}NBr]_2,H_2PtCl_6$, was obtained in a similar way by using platinic chloride. It is a yellow powder, which was washed with dry ether and dried at 105°. The specimen was evidently not quite pure:

0·0603 gave 0·0108 Pt. Pt = 17·91.

$C_{42}H_{26}N_2Cl_6Br_2Pt$ requires Pt = 17·31 per cent.

4. *Replacement of the Bromine in Monobromodinaphthacridine by Hydrogen.*

In order to prove the constitution of monobromodinaphthacridine, it was necessary to replace the bromine by hydrogen. The reduction took place readily by the action of an alcoholic solution of stannous chloride on the base partly dissolved and partly suspended in alcohol. Some tin and free hydrochloric acid were added, and the mixture was boiled for several hours under a reflux condenser, when a green substance gradually formed. When cold, the liquid was removed by filtration, and the green substance was separated mechanically from the residual tin. This green substance was boiled with methylated spirit, in which it was moderately soluble, then treated with potassium hydroxide, boiled, mixed with water, and the yellow, flocculent precipitate obtained was dissolved in aqueous pyridine. The filtered solution deposited orange crystals melting at 243°. They were identified as bis-$\begin{smallmatrix}\beta\text{-N-}\beta\\ |\\ \alpha\text{-CH}\alpha\end{smallmatrix}$-dinaphthacridine dihydride (Senier and Austin, Trans., 1906, 89, 1398), which is known to give a green hydrochloride.

The bromodinaphthacridine is evidently therefore a derivative of  $\begin{matrix}\beta\text{-N-}\beta \\ | \\ \alpha\text{-CH}\alpha\end{matrix}$-dinaphthacridine (Reed).

5. *Interaction of Methylene Dichloride and* 1-*Nitro-2-naphthylamine.*

When 1-nitro-2-naphthylamine was heated to 210° in a closed tube with methylene dichloride for one hour, it was found that no reaction had taken place, for the original substance was recovered unchanged. Another attempt was made by heating the tube to 250—260° for two hours, when the contents of the tube were completely charred, although acridines are stable at this temperature.

QUEEN'S COLLEGE,
GALWAY.

VII.—*The Direct Interaction of Aryl Halides and Magnesium.*

By JAMES FREDERICK SPENCER AND ELEANOR MARGUERITE STOKES.

IN the course of a series of reactions involving the use of the Grignard reagent, we obtained evidence which led us to doubt the necessity of the presence of ether or any catalyst in the preparation of magnesium aryl halogen compounds. Preliminary experiments showed that aryl iodides and magnesium react, on heating, with the formation of magnesium aryl iodides, which in view of the subsequent action of water must be constituted according to the type $R\cdot Mg\cdot I$.

The reaction took place with the evolution of a large amount of heat, and was generally complete in two to three minutes; on the addition of water, after cooling, the parent hydrocarbon was regenerated with the evolution of heat:

$$RMgI + H_2O = R\cdot H + Mg(OH)I.$$

The ease with which the combination occurred indicated that this was possibly a reaction suitable for removing halogens from cyclic compounds, and so capable of being used as a means of orientation in the case of substituted compounds.

With the object of testing the suitability of the reaction for such determinations, we have studied the action of magnesium with a number of aromatic halogen substitution products, and have found that it is possible to remove iodine and bromine from such compounds almost quantitatively, and to obtain a large yield of the parent substance as product of the reaction.

Thus *m*-bromoaniline gave a yield of 90 per cent. of the theoretical quantity of aniline, and *p*-bromophenol gave 40—50 per cent. of the theoretical yield of phenol.

Halogen acids and nitro-compounds containing halogens did not yield the corresponding acids and nitro-hydrocarbons. In the case of the acids, carbon dioxide was evolved, and with the nitro-compounds, nitrogen peroxide was evolved, which immediately reacted with the magnesium, giving rise to so much heat that the compound was completely charred, and, indeed, in one experiment the test-tube melted.

Halogen derivatives of naphthalene react in the same way with magnesium, *a*-bromonaphthalene yielding 70—80 per cent. of naphthalene.

Similarly, monobromoacenaphthene gave a yield of about 50 per cent. of the theoretical quantity of acenaphthene when treated in the same way.

This reaction does not seem to be general for chloro-substitution products; out of six substances investigated, namely, benzylidene chloride, *o*- and *p*-chlorophenol, *a*-chloronaphthalene, *p*-chlorotoluene, and *o*-chloroaniline, a reaction was found to take place only in the case of *o*-chloroaniline; in this instance, a large yield of aniline was obtained. Iodobènzene and bromobenzene require special note, for with these compounds it was found that the initial reaction proceeded in two directions, as indicated by the equations:

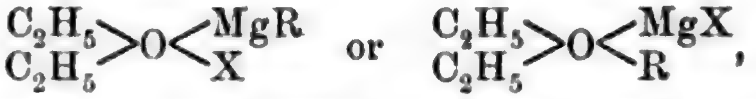
$$(1)\ C_6H_5I + Mg = C_6H_5{\cdot}Mg{\cdot}I.$$
$$(2)\ 2C_6H_5I + Mg = C_6H_5{\cdot}C_6H_5 + MgI_2.$$

The products, benzene and diphenyl, were present in quantities which indicated that the reaction represented by (1) had taken place with about 45 per cent. of the iodobenzene, and the reaction represented by equation (2) with about 55 per cent. of the iodobenzene. The formation of diphenyl was observed by Tissier and Grignard (*Compt. rend.*, 1901, **132**, 32) when carrying out the Grignard reaction under ordinary conditions.

We have done little up to the present with aliphatic compounds, but preliminary experiments have shown that methyl iodide, methylene iodide, trimethylene iodide, and *iso*propyl iodide do not react at all with magnesium when the two substances are heated together. Monobromosuccinic acid, however, does react, and the action commences without initial heating after the substances have been mixed for about two minutes. The product on treatment with water yields succinic acid.

On treating the magnesium aryl compounds with water, we obtained derivatives which may be used for deciding the position of substituting groups; they can, however, also be used for purposes of synthesis. For example, magnesium phenyl iodide, prepared by the method indicated, was ground in a mortar with a little absolute ether and an excess of solid carbon dioxide for about five minutes, the product of this treatment yielded about half the theoretical quantity of benzoic acid on the addition of dilute hydrochloric acid. In the absence of ether, the yield of benzoic acid was much reduced.

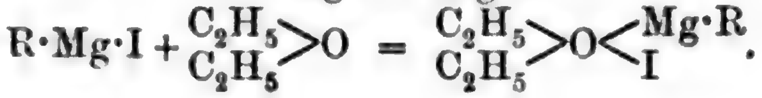
This reaction, effected without the use of a catalyst, indicates that ether is not absolutely necessary for the reaction, and the Grignard compounds are not necessarily formed through oxonium compounds of the type:



$$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}{>}O{<}\begin{matrix}MgR\\X\end{matrix} \quad \text{or} \quad \begin{matrix}C_2H_5\\C_2H_5\end{matrix}{>}O{<}\begin{matrix}MgX\\R\end{matrix},$$

but rather, the view put forward by Tschelinzeff (*Ber.*, 1905, **38**, 3664) is the more correct one, namely, that the addition occurs first between the iodide and the magnesium, and this then forms an addition compound with ether:

$$RI + Mg = R{\cdot}Mg{\cdot}I.$$



$$R{\cdot}Mg{\cdot}I + \begin{matrix}C_2H_5\\C_2H_5\end{matrix}{>}O = \begin{matrix}C_2H_5\\C_2H_5\end{matrix}{>}O{<}\begin{matrix}Mg{\cdot}R\\I\end{matrix}.$$

EXPERIMENTAL.

Interaction of Iodobenzene and Magnesium.—Dry iodobenzene (40 grams) was mixed with dry magnesium powder (9 grams) in a small, hard, round-bottomed flask fitted with an air condenser. The mixture was carefully warmed over a free flame to the boiling point of the iodobenzene; after boiling for about a minute, the reaction commenced, and proceeded without any additional heating. The product was a light grey, homogeneous mass, which was slowly decomposed by the moisture of the air, forming benzene. When the mass had cooled, cold water was slowly added to it; this brought about a decomposition which was accompanied by the evolution of heat. As soon as the decomposition was complete, the products were distilled with steam, when benzene, diphenyl, and unchanged iodobenzene were found in the distillate. The yield of benzene was 44 per cent., and of diphenyl 54 per cent., of that required by theory.

The melting point of the diphenyl (70°) was unchanged after mixture with an equal weight of pure diphenyl.

Interaction of Bromobenzene and Magnesium.—In this case, the reaction did not occur at all readily, it being necessary to boil the mixture of bromobenzene and magnesium for about fifteen minutes before combination took place. The organic products and yields were the same as in the case of iodobenzene.

Interaction of p-*Iodotoluene and Magnesium.*—*p*-Iodotoluene (15 grams) and magnesium powder (2 grams) were mixed and gently warmed in a hard glass flask fitted with an air condenser. As soon as the boiling point of the iodotoluene was reached, the reaction also commenced, and proceeded without further heating; it was, however, not as violent as with iodobenzene. The product was a light grey mass, which was treated with water and distilled in steam. The distillate was extracted, dried, and fractionated, and shown to consist of toluene. The yield was 87 per cent., and a small quantity of unchanged *p*-iodotoluene was also recovered.

Interaction of o-*Bromotoluene and Magnesium.*—The interaction of these two substances took place in exactly the same way as in the case of *p*-iodotoluene. The product was the same, and the yield was equally good.

Interaction of m-*Bromoaniline and Magnesium.*—Dry *m*-bromoaniline (15 grams) was mixed with magnesium powder (4 grams) and heated in the same way as the foregoing mixtures; after two minutes, a most violent reaction took place. A yellow, solid mass was obtained, which reacted so violently with water that the liquid boiled. The whole mass was then distilled in steam, and the oil which passed over was extracted and fractionated. A yield of 90 per cent. of aniline was obtained.

Interaction of o-*Chloroaniline and Magnesium.*—This reaction took place extremely readily when heat was employed, and a good yield of aniline was produced.

Interaction of p-*Bromophenol and Magnesium.*—*p*-Bromophenol (8 grams) was mixed with magnesium powder (2 grams) and heated, the reaction commencing suddenly after about two to three minutes' heating. The product, a light grey, solid mass, was treated with water and distilled in steam, when a yield of 40 to 50 per cent. of phenol was obtained.

When tribromophenol was substituted for phenol, the reaction took place with extreme violence and evolution of heat, causing the tube to soften. The products contained less bromine than the original tribromophenol, for on the addition of bromine water to the solution a yellowish-white precipitate of tribromophenol was formed, but further identification was impossible, nor could the vigour of the reaction be lessened.

Interaction of a-*Bromonaphthalene and Magnesium.*—a-Bromonaphthalene (20 grams), mixed with magnesium powder (4 grams), was heated to boiling point, when a vigorous reaction commenced, which completed itself without any further heating. The product was a white and apparently crystalline mass. When cold, the addition of water was attended by great evolution of heat, and the presence of naphthalene was at once evident from its odour. The mass was then distilled in steam, when a 72 per cent. yield of naphthalene was obtained. The yield was improved by the use of excess of magnesium; thus, whilst one atomic proportion of magnesium furnished a yield of 44 per cent. of the theoretical, from three times the quantity a yield of 72 per cent was obtained. The change in the yield is due to the smaller amount of the bromo-compound escaping reaction.

Interaction of Bromoacenaphthene and Magnesium.—About 1 gram of bromoacenaphthene was mixed with excess of magnesium powder and heated over the free flame. The reaction did not commence for about five minutes, and then proceeded quietly. Water was then added to the product, but action took place only on warming. This was in all probability due to the fact that the magnesium acenaphthyl bromide was protected from its action by being coated with unchanged bromoacenaphthene. The products after treatment with water were extracted with alcohol, and the acenaphthene formed crystallised out in good yield.

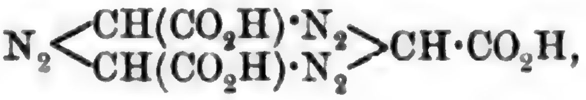
The investigation of this reaction is being continued.

CHEMICAL LABORATORY,
BEDFORD COLLEGE,
BAKER STREET, W.

VIII.—*The Triazo-Group. Part I. Triazoacetic Acid and Triazoacetone (Acetonylazoimide).*

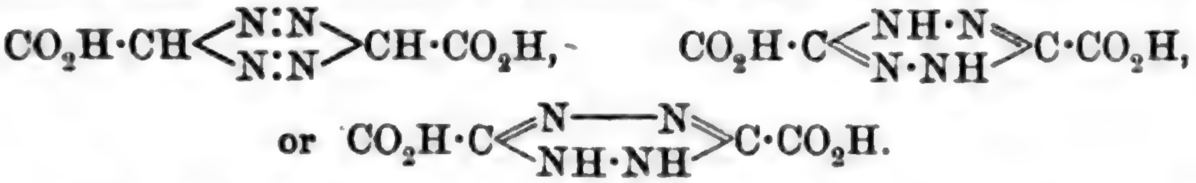
By MARTIN ONSLOW FORSTER and HANS EDUARD FIERZ.

DESPITE the variety of triazo derivatives which have been investigated, principally by Griess, Curtius, Noelting, and their collaborators during the past forty years, one class of these compounds would appear to have escaped examination; we refer to those types in which the triazo-group has replaced hydrogen in carboxylic acids, ketones, aldehydes, and alcohols of the aliphatic series. So far as we have been able to ascertain, the only triazo-ketone to be met with in the literature is camphorylazoimide (Trans., 1905, **87**, 826), and it is chiefly in connexion with this compound that our attention has been drawn to the subject. The "triazoacetic acid" described by Curtius and Lang (*J. pr. Chem.*, 1888, [ii], **38**, 532), at first regarded as having the constitution:



$$N_2{<}\begin{matrix}CH(CO_2H)\cdot N_2\\ CH(CO_2H)\cdot N_2\end{matrix}{>}CH\cdot CO_2H,$$

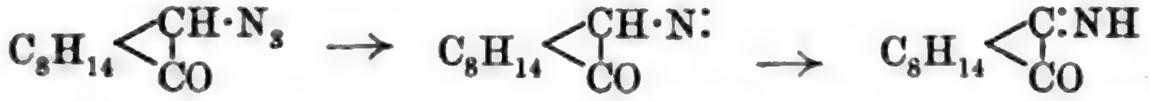
is now recognised as a bimolecular polymeride of diazoacetic acid; entitled bisdiazoacetic acid, it is variously represented as



$$\mathrm{CO_2H{\cdot}CH}{<}\genfrac{}{}{0pt}{}{\mathrm{N{:}N}}{\mathrm{N{:}N}}{>}\mathrm{CH{\cdot}CO_2H},\qquad \mathrm{CO_2H{\cdot}C}{<}\genfrac{}{}{0pt}{}{\mathrm{NH{\cdot}N}}{\mathrm{N{\cdot}NH}}{>}\mathrm{C{\cdot}CO_2H},$$

$$\text{or}\quad \mathrm{CO_2H{\cdot}C}{<}\genfrac{}{}{0pt}{}{\mathrm{N{-\!-\!-}N}}{\mathrm{NH{\cdot}NH}}{>}\mathrm{C{\cdot}CO_2H}.$$

In the present communication, we describe triazoacetic acid, $N_3{\cdot}CH_2{\cdot}CO_2H$, its amide, and ethyl ester, along with the simplest triazo-ketone, acetonylazoimide or triazoacetone, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}N_3$. The last-named substance is the true analogue of camphorylazoimide, which it recalls in respect of its behaviour towards potash; the action of alkali on the simpler molecule is very vigorous, alcoholic potash liberating nitrogen from acetonylazoimide almost explosively, whilst the aqueous alkali, even when very dilute (2 per cent.), sets up a brisk effervescence. There is a distinction, however, between camphorylazoimide and triazoacetone in regard to the quantitative aspect of the change. We have shown that exactly two-thirds of the nitrogen is liberated from the camphor derivative, which passes into the imine of camphorquinone:



$$\mathrm{C_8H_{14}}{<}\genfrac{}{}{0pt}{}{\mathrm{CH{\cdot}N_3}}{\mathrm{CO}} \longrightarrow \mathrm{C_8H_{14}}{<}\genfrac{}{}{0pt}{}{\mathrm{CH{\cdot}N{:}}}{\mathrm{CO}} \longrightarrow \mathrm{C_8H_{14}}{<}\genfrac{}{}{0pt}{}{\mathrm{C{:}NH}}{\mathrm{CO}},$$

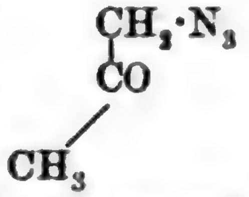
but the gasometric study of the alteration which acetonylazoimide undergoes with alkali shows that subsidiary to the change,

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}N_3 \longrightarrow CH_3{\cdot}CO{\cdot}CH{:}NH \longrightarrow CH_3{\cdot}CO{\cdot}CH{:}O,$$

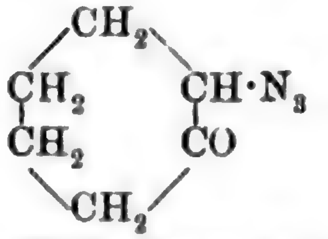
there occurs, to the extent of, roughly, 15 per cent., elimination of hydrazoic acid,

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}N_3 + H_2O = CH_3{\cdot}CO{\cdot}CH_2{\cdot}OH + HN_3,$$

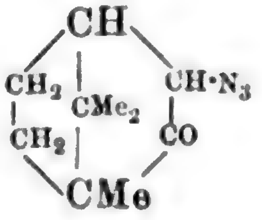
which does not take place when camphorylazoimide is treated with boiling alkali. This difference in behaviour probably owes its origin to the absence of the cycloid structure, which renders the camphor derivative more stable, and also to the more hydrogenised condition of the carbon atom to which the triazo-group is attached in acetonylazoimide, as well as to the comparative freedom of the unsubstituted methyl group, because a preliminary experiment with 2-triazo*cyclo*hexanone has indicated that in this case, also, both changes proceed simultaneously:



Yields nitrogen and hydrazoic acid.

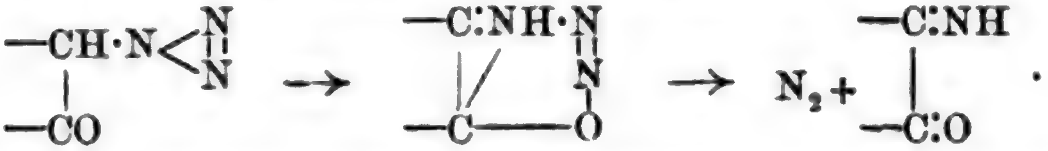


Yields nitrogen and hydrazoic acid.

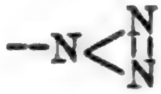


Yields nitrogen only.

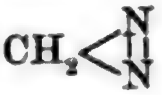
The facility with which nitrogen is eliminated from these compounds appears to depend on the immediate neighbourhood of the ketonic and triazo-groups, and leads us to suggest, as a possible explanation, that the action of alkali is such as to bring about the formation of an unstable ring-system from which nitrogen is forthwith liberated:



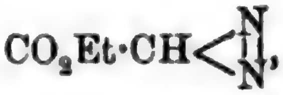
Accepting the common view of the triazo-group, and comparing it with the diazo-complex as occurring in diazomethane and diazoacetic ester,



$$-N\Big<\begin{matrix}N\\ \| \\ N\end{matrix}$$

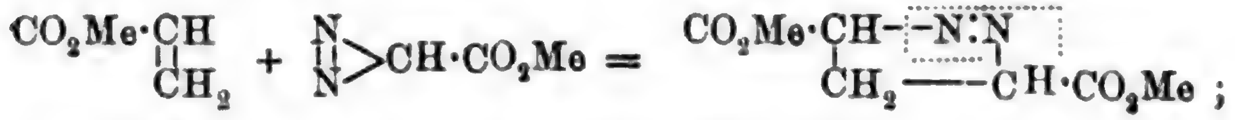


$$CH_2\Big<\begin{matrix}N\\ \| \\ N\end{matrix}$$

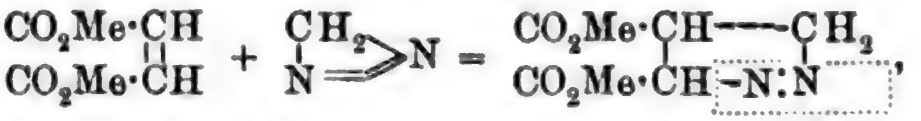


$$CO_2Et\cdot CH\Big<\begin{matrix}N\\ \| \\ N\end{matrix},$$

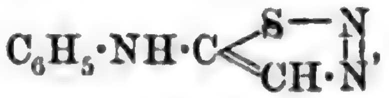
it will be recognised that two-thirds of the nitrogen in the first-named radicle stands in that relation to the remainder which is borne by the nitrogen in alphatic diazo-compounds to the carbon with which it is combined. Now there exists a considerable body of evidence to show that the nitrogen in diazomethane and diazoacetic ester is capable of taking part in additive action, the products parting easily with the element in question. For instance, Buchner (*Annalen*, 1893, **273**, 214; compare also Buchner and Papendieck, *loc. cit.*, 232 and 246; Buchner and Witter, *loc. cit.*, 239) found that when ethyl diazoacetate acts on the esters of unsaturated acids, pyrazolinedicarboxylic esters are produced, which lose nitrogen when heated, yielding trimethylenedicarboxylic esters:



von Pechmann, again (*Ber.*, 1894, **27**, 1890), obtained methyl pyrazoline-4:5-dicarboxylate by the interaction of diazomethane and methyl fumarate,

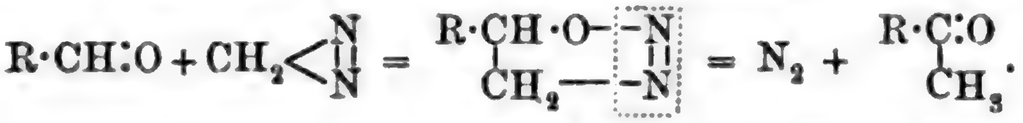


the pyrazolinecarboxylic esters being here represented in their pseudo-form to indicate more clearly the loss of nitrogen. Another ring-system which readily parts with the element arises from diazomethane and thiocarbimides, von Pechmann and Nold (*Ber.*, 1896, **29**, 2588) having shown that phenylaminothiodiazole,



behaves in this manner when fused, whilst the recent conversion of aldehydes into methyl ketones by the action of diazomethane

(Schlotterbeck, *Ber.*, 1907, **40**, 479) has been explained with some plausibility by assuming the intermediate formation of furodiazoles,



$$\mathrm{R{\cdot}CH{:}O + CH_2{<}\begin{array}{c}N\\ \|\\ N\end{array} = \begin{array}{l}R{\cdot}CH{\cdot}O{-}{-}N\\ \phantom{R{\cdot}}|\qquad\quad \|\\ \phantom{R{\cdot}}CH_2{-}{-}{-}N\end{array} = N_2 + \begin{array}{l}R{\cdot}C{:}O\\ \phantom{R{\cdot}}|\\ \phantom{R{\cdot}}CH_3\end{array}.}$$

Hence the possibility of mutual satisfaction of affinity between the carbonyl and triazo-groups appears by no means remote, and is independent of the alternative representations,

$$-\mathrm{N{:}N{:}N} \text{ and } -\mathrm{CH{:}N{:}N},$$

which might be used for the azoimide complex and aliphatic diazo-radicle respectively.

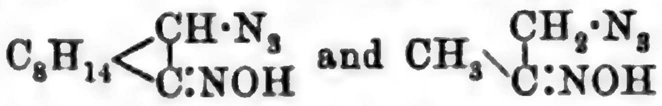
Another argument in favour of this explanation may be drawn from the behaviour of triazoformic, as compared with that of triazoacetic, ester. When ethyl triazoformate is treated with aqueous potash, the substance is promptly hydrolysed, nitrogen being eliminated exclusively in the form of hydrazoic acid:

$$\mathrm{N_3{\cdot}CO_2{\cdot}C_2H_5 + H_2O = HN_3 + CO_2 + C_2H_5{\cdot}OH};$$

here there is no hydrogen attached to the carbon atom with which the triazo-group is combined, and consequently the tendency towards ring-formation as indicated above cannot find expression, whereas triazoacetic acid so far resembles triazocamphor as to yield nitrogen when boiled with excess of potash, unaccompanied by hydrazoic acid,

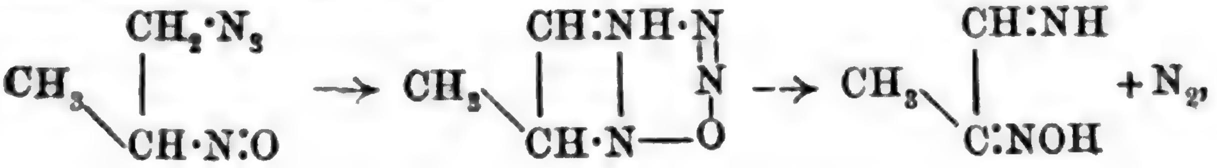
$$\mathrm{N_3{\cdot}CH_2{\cdot}CO_2H} \longrightarrow \mathrm{N_2 + NH{:}CH{\cdot}CO_2H},$$

although the negative hydroxyl group certainly exerts a powerful retarding influence on the change. Whilst, however, this hypothesis of potential ring-formation appears to us a reasonable one, difficulty arises in connexion with triazoacetoxime and the oxime of camphorylazoimide. It has been shown that the latter substance yields hydrazoic acid instead of nitrogen with alcoholic potash (Trans., 1907, **91**, 874), but we now find that triazoacetoxime furnishes both hydrazoic acid and nitrogen with the utmost readiness, and a comparison of the formulæ:



$$\mathrm{C_8H_{14}{<}\begin{array}{l}CH{\cdot}N_3\\ |\\ C{:}NOH\end{array}} \text{ and } \mathrm{CH_3{\diagdown}\begin{array}{l}CH_2{\cdot}N_3\\ |\\ C{:}NOH\end{array}}$$

does not suggest an explanation of this apparent discrepancy. Triazoacetoxime is a very labile substance, however, and cannot be distilled, even under 2 mm. pressure, without undergoing decomposition; moreover, we believe it has a tendency to undergo transformation into the nitroso-modification, and consequently it may be supposed that the liberation of nitrogen is due to intermediate association of the triazo- and nitroso-groups,



$$\mathrm{CH_3{\diagdown}\begin{array}{l}CH_2{\cdot}N_3\\ |\\ CH{\cdot}N{:}O\end{array}} \longrightarrow \mathrm{CH_3{\diagdown}\begin{array}{l}CH{:}NH{\cdot}N\\ |\qquad\ |\quad\ \|\\ |\qquad\ |\quad\ N\\ CH{\cdot}N{-}O\end{array}} \longrightarrow \mathrm{CH_3{\diagdown}\begin{array}{l}CH{:}NH\\ |\\ C{:}NOH\end{array}} + \mathrm{N_2},$$

opportunity for which does not present itself in the case of the camphoryl derivative.

The properties of triazoacetic ester naturally invite comparison with those of the corresponding diazo-compound, prepared by Curtius, and the contrast between the two substances brings out once more the stability of the triazo-group as compared with the diazo-complex. Boiling water, iodine, mercuric oxide, and ammoniacal silver oxide leave the ester unchanged, and sodium does not dissolve in the cold substance; it is, moreover, colourless, and the odour is very faint. Furthermore, triazoacetic ester may be hydrolysed to the acid, which is a well-defined substance, and does not decompose below 100°, whereas attempts to liberate diazoacetic acid by passing carbon dioxide through the hydrolysed ester result in liberation of nitrogen, whilst concentrated aqueous alkalis induce simultaneous hydrolysis and polymerisation, leading to bisdiazoacetic acid.

We are engaged in studying the triazo-derivatives of other typical members of the aliphatic series, including alcohols, aldehydes, ketones, and esters; such compounds have been prepared from methyl ethyl ketone, malonic ester, and acetoacetic ester, and we hope to describe these in a subsequent communication.

EXPERIMENTAL.

Triazoacetic Acid, $N_3 \cdot CH_2 \cdot CO_2H$.

Fifty grams of triazoacetic ester were shaken with a 20 per cent. solution of potassium hydroxide containing 21 grams, this being a slight deficit from one molecular proportion; the temperature rose and the oil disappeared slowly, but there was no liberation of gas. After being twice extracted with ether, the neutral solution was treated with the calculated amount of sulphuric acid and extracted fifteen times with ether, which, when dried with ignited sodium sulphate, left a very pale yellow, oily liquid on evaporation. This was heated in boiling water during one hour under 2 mm. pressure, when the acid was found to be sufficiently anhydrous to solidify in melting ice, but there was no distillation at this temperature, and it was not considered safe to heat the substance more strongly.

Triazoacetic acid crystallises in hygroscopic, glassy plates, and melts at about 16°. It has a very faint odour, suggesting that of butyric acid without the pungent effect; the substance is a strong acid, and feels greasy when rubbed between the fingers. On a hot plate, the acid detonates with a moderate explosion and takes fire, but when it is heated in a capillary tube a violent detonation occurs. It does not reduce ammoniacal silver oxide, even on boiling the solution.

The analysis of triazoacetic acid and ester has presented unusual obstacles, and more than twenty attempts have been made to obtain satisfactory results. The principal difficulty lies in the fact that when combustion is conducted under ordinary conditions, methane appears among the products, whilst adopting the device which has been suggested to meet this drawback, namely, substitution of lead chromate for copper oxide and mixing the substance with cuprous chloride (Dunstan and Carr, Proc., 1896, **12**, 48, and Haas, Trans., 1906, **89**, 570), low results were obtained consequent on the production of methylamine. In the case of the acid, combustion for percentage of carbon and hydrogen was finally carried out in a tube containing platinised asbestos, an attempt being made to maintain throughout the operation a large excess of oxygen, which was used instead of air; for the purpose of estimating nitrogen, advantage was taken of the fact that when potassium triazoacetate is heated with excess of potash the triazo-group undergoes disruption, and accordingly the weighed substance was mixed with 20 per cent. aqueous potash before being placed in the combustion tube:

0·3306 gave 0·2913 CO_2 and 0·0892 H_2O. C = 24·03; H = 2·99.
0·0947 „ 34·25 c.c. of nitrogen at 18·5° and 747 mm. N = 41·64.
$C_2H_3O_2N_3$ requires C = 23·76; H = 2·97; N = 41·58 per cent.

In view of the violence with which aromatic azoimides lose nitrogen when treated with concentrated sulphuric acid, the behaviour of the agent towards triazoacetic acid is remarkable; when mixed with concentrated sulphuric acid on a watch-glass, no change takes place immediately, and only on vigorous stirring with a glass rod does gas appear, very slowly at first, but quickly increasing in briskness.

Estimation of molecular weight was conducted in benzene and in phenol. In the former solvent, 221 units represents the average of three experiments, whilst in phenol the mean of four amounted to 99 units, the solution being brown; the formula $C_2H_3O_2N_3$ requires 101 units.

Salts of Triazoacetic Acid.—The *silver* salt, $C_2H_2O_2N_3Ag$, obtained as a curdy precipitate on adding silver nitrate to a neutral solution of potassium triazoacetate, may be crystallised from boiling water in presence of a few drops of dilute nitric acid, separating in colourless, lustrous needles. An attempt to estimate the silver by cautious evaporation with nitric acid having led to a slight detonation, a weighed quantity of the substance was reduced with ammonium sulphide, the silver sulphide thereby precipitated being converted into silver. For the purpose of estimating nitrogen, the salt was mixed with 20 per cent. potash before being placed in the tube:

0·2661 gave 0·1385 Ag. Ag = 52·05.
0·1923 ,, 34·4 c.c. of nitrogen at 19° and 745 mm. N = 20·50.
$C_2H_2O_2N_3Ag$ requires Ag = 51·92 ; N = 20·20 per cent.

When heated on an iron plate, the substance detonates mildly and burns brightly.

An attempt to prepare the copper salt led to a curious result. Having noticed that copper sulphate develops a deep green coloration when mixed with potassium triazoacetate, copper oxide was dissolved in an aqueous solution of the free acid. It was noticed, however, that this solution steadily liberates gas when heated on the water-bath, and, although the liquid may be concentrated at 40°, an attempt to obtain crystals of the copper salt by leaving the liquid in a desiccator failed, because at a high concentration gas was evolved, even at the ordinary temperature. A dark green, hygroscopic powder finally remained, and, on warming an aqueous solution of this product with dilute potash, it remained momentarily clear, but suddenly precipitated cuprous oxide and liberated ammonia.

The potassium salt is freely soluble in water, and is precipitated by concentrated potash. A neutral, moderately dilute solution is surprisingly stable, and may be boiled without evolving gas, but on adding to the hot liquid some 40 per cent. potash, torrents of gas are liberated, followed, after a momentary pause, by another rush of gas, consisting of nitrogen and ammonia, and the effervescence is continued in this characteristic fashion by further addition of alkali. We have made several attempts to isolate the products of this change, which should include glyoxylic acid, but hitherto we have been able to recognise only oxalic acid, which probably arises from glyoxylic acid by the action of potash. When the potassium salt has been treated with excess of alkali in the manner indicated above, the liquid deposits crystals on cooling, but the composition of this product appears to vary considerably according to the conditions of the experiment. On one occasion, a small quantity of a substance was obtained which left no residue on evaporation with concentrated sulphuric acid, and appeared to be an ammonium salt; it reduced ammoniacal silver oxide and Fehling's solutions immediately without warming, but this property disappeared on boiling with potash, and the reaction is being studied therefore more fully.

A neutral solution of potassium triazoacetate gives a lustrous, crystalline precipitate with lead nitrate, and a deep red coloration with ferric chloride.

Ethyl Triazoacetate, $N_3\cdot CH_2\cdot CO_2\cdot C_2H_5$.

Two hundred grams of ethyl chloroacetate and 100 grams of alcohol were heated under reflux during three hours with 120 grams of sodium azide, and sufficient water to maintain the salt in solution; a current of steam was then passed through the liquid, from which the ester was quickly removed. On diluting the distillate with water, adding a considerable quantity of crystallised sodium acetate, and allowing the heavy oil to separate, 190 grams of the substance were obtained, and this was shaken twice with water, dried with calcium chloride, and distilled under 2 mm. pressure, when it boiled to the last few drops at 44—46°.

The difficulties presented by the analysis of this ester have been mentioned above, and after eight attempts, the indicated results of which vary between 19·8 and 34·3 per cent. of nitrogen, we are still unable to record a satisfactory estimation of this element; by the use of platinised asbestos, however, fairly concordant determinations of carbon and hydrogen have been obtained, although these have been usually too high, owing to the difficulty of avoiding the formation of nitrous fumes, even in presence of silver gauze:

0·1571 gave 0·2100 CO_2 and 0·0790 H_2O. C = 36·30; H = 5·62.
$C_4H_7O_2N_3$ requires C = 37·21; H = 5·43 per cent.

We are indebted to Dr. Joshua for an independent estimation of carbon by oxidation with a mixture of sulphuric and chromic acids:

0·1202 gave 0·1620 CO_2. C = 36·76 per cent.

It happens, unfortunately, that the gasometric estimation of nitrogen eliminated by concentrated sulphuric acid, hot potash, or stannous chloride cannot be used to supplement the above analytical data regarding the ester, because the action in each case takes an abnormal course, and the percentage of gas evolved by these agents agrees more closely with half the azidic nitrogen (16·3 per cent.) than with two-thirds (21·7 per cent.). So regular is this discrepancy from the expected result that we became suspicious, before the analytical difficulties were surmounted, regarding the identity of the ester, as it seemed possible that the triazo-group had conferred on acetic ester the capacity to form an alcoholate, because it happens by chance that two-thirds of the nitrogen required by the formula,

$$N_3\cdot CH_2\cdot C(OEt)_2\cdot OH$$

amounts to 16·0 per cent., or, roughly, half the nitrogen content of the simple ester. Accordingly, a specimen of triazoacetic ester was prepared by heating 50 grams of ethyl chloroacetate under reflux with sodium azide dissolved in water, but the product was found to correspond in every respect with the ester prepared in presence of alcohol; the action proceeds in the same way, but is much more sluggish than when alcohol is used. The abnormal behaviour indicated above still awaits explanation, therefore, and we hope to furnish this later.

Triazoacetic ester is a limpid, colourless oil, having a faint, sweet odour, more suggestive of chloroform than of ethyl acetate, the resemblance to the latter becoming more marked in steam, with which the substance is readily volatile; when inhaled for some seconds, the vapour produces a throbbing sensation in the head, and slight palpitation of the heart. On mixing with concentrated sulphuric acid, there is no effervescence at first, but, on stirring vigorously, gas is liberated slowly, the disengagement becoming ultimately quite brisk; with stannous chloride dissolved in concentrated hydrochloric acid, nitrogen is evolved immediately. When the ester is shaken and warmed with 10 per cent. caustic potash, it is quickly hydrolysed, forming a clear solution of potassium triazoacetate, but concentrated alkali (40 per cent.) appears to leave the substance unchanged, unless alcohol is added or the temperature raised. Freshly-cut sodium does not dissolve in it unless the liquid is heated, when vigorous action takes place; the substance is indifferent towards mercuric oxide and a solution of iodine in potassium iodide.

The specific gravity of triazoacetic ester is 1·127 compared with water at 20°. An estimation of molecular weight in benzene gave 119, 125, and 127 units, the formula $C_4H_7O_2N_3$ requiring 129.

Triazoacetamide, $N_3{\cdot}CH_2{\cdot}CO{\cdot}NH_2$.

When shaken with aqueous ammonia, the ester dissolved, and, on evaporating on the water-bath, a pale red liquid remained which solidified on cooling; this was drained on earthenware, and recrystallised twice from hot benzene:

0·1411 gave 68·4 c.c. of nitrogen at 20° and 758 mm. N = 56·30.
$C_2H_4ON_4$ requires N = 56·00 per cent.

Triazoacetamide forms tough, lustrous, colourless needles, frequently exceeding an inch in length, and melting at 58°; it is readily soluble in water and in alcohol, but is most conveniently crystallised from hot benzene, in which it is moderately soluble, whilst boiling petroleum also dissolves it, but less freely. When thrown on a hot plate, it detonates feebly and takes fire.

The substance is unusually resistant towards concentrated sulphuric acid, with which it must be warmed to about 50° before gas is liberated; cold 60 per cent. aqueous potash, however, attacks it immediately, torrents of nitrogen and ammonia being liberated, whilst more dilute solutions of alkali disrupt the triazo-group very slowly. An aqueous solution of the amide dissolves yellow mercuric oxide on boiling, but the resulting compound, unlike mercury acetamide, does not lose the metal when treated with hydroxylamine hydrochloride, a precipitate being formed only on adding alkali, when effervescence takes place (compare Trans., 1898, **73**, 785).

Ethyl Triazoformate, $N_3 \cdot CO_2 \cdot C_2H_5$.

Methyl azoimidocarbonate was prepared by Curtius and Heidenreich (*J. pr. Chem.*, 1895, [ii], **52**, 454) from ammonium azoimide and methyl chlorocarbonate, and, in order to compare the condition of the triazo-group in this type of compound with the behaviour of the same complex occurring in the acetic series, we have examined the corresponding ethyl ester, which was prepared by agitating 50 grams of ethyl chlorocarbonate with an aqueous solution of sodium azide containing 35 grams until the pungent odour of the original material was no longer perceptible; the heavy oil was then removed, dried with sodium sulphate, and distilled under 2 mm. pressure, when it boiled steadily at 25°.

The colourless, limpid ester has sp. gr. 1·118 compared with water at 18°, and boils at 114° under 769 mm. pressure, but is liable to explode; the odour is more powerful than that of triazoacetic ester, and the disagreeable effects of inhaling the vapour are much more marked. It may be mixed with concentrated sulphuric acid or 40 per cent. potash without evolving gas, but the alkali hydrolyses it completely to hydrazoic acid, alcohol, and carbonic acid; it is therefore impossible to produce triazoformic acid, or even the salts, because a deficit of alkali merely leaves the corresponding amount of ester unchanged. Alcoholic ammonium sulphide reduces ethyl triazoformate to urethane, nitrogen being set free.

Triazoacetone (*Acetonylazoimide*), $N_3 \cdot CH_2 \cdot CO \cdot CH_3$.

The monochloroacetone required for the production of triazoacetone was prepared by Fritsch's method (*Annalen*, 1894, **279**, 313), which we have found to yield excellent results.

One hundred grams of chloroacetone (b. p. 119—121°) were shaken with a concentrated aqueous solution of sodium azide containing 80 grams, to which a few drops of glacial acetic acid had been added; after twenty-four hours, the pungent odour of chloroacetone being no longer perceptible, the oil was extracted with ether, dried with sodium sulphate, and distilled under 2 mm. pressure. The product, weighing 90 grams, was shaken with freshly-ignited sodium sulphate, and again distilled under 2 mm. pressure, the major portion boiling at 54°, and having sp. gr. 1·123 compared with water at 18°:

0·2398 gave 0·3204 CO_2 and 0·1132 H_2O. C = 36·44 ; H = 5·24.
0·1685 „ 61·1 c.c. of nitrogen at 19° and 761 mm. N = 42·45.
$C_3H_5ON_3$ requires C = 36·36 ; H = 5·05 ; N = 42·42 per cent.

Freshly-distilled triazoacetone is a colourless, highly refractive liquid having a faint odour, but after a few days, even when preserved in a well-stoppered bottle and protected from light, the odour of carbylamine is noticeable in the specimen, which has become yellow. The substance exhibits no tendency to solidify, remaining quite limpid in a freezing mixture; it is sparingly soluble in water, and very readily volatile in steam. When dropped on a hot plate, triazoacetone explodes, and burns with a brilliant flame; concentrated sulphuric acid decomposes the substance immediately, liberating nitrogen.

Action of Alkali.—When triazoacetone is treated with concentrated aqueous potash (40 per cent.), nitrogen is liberated with almost explosive violence, and the liquid becomes red; even with a 1 per cent. solution of the alkali, gas evolution is quite brisk, and several concordant estimations of the nitrogen evolved during the change indicated that this amounted to roughly 4 per cent. less than two-thirds:

0·1550 gave 33·4 c.c. of nitrogen at 22° and 761 mm. N = 24·3.
$C_3H_5ON_3$ requires 2/3N = 28·3 per cent.

By decomposing 5 grams of the triazo-ketone at one time, steaming the product while alkaline, then adding dilute sulphuric acid and distilling again, we were able to show that the deficit indicated above is due to simultaneous production of hydrazoic acid, which was easily recognised in the acid distillate. Excepting ammonia, however, the other products of the changes involved are not easily identified. The fact that nitrogen, ammonia, and hydrazoic acid are eliminated, indicates that the following decomposition occurs:

$$\text{I. } N_3{\cdot}CH_2{\cdot}CO{\cdot}CH_3 = N_2 + NH{:}CH{\cdot}CO{\cdot}CH_3.$$
$$\text{II. } NH{:}CH{\cdot}CO{\cdot}CH_3 + H_2O = NH_3 + O{:}CH{\cdot}CO{\cdot}CH_3.$$
$$\text{III. } N_3{\cdot}CH_2{\cdot}CO{\cdot}CH_3 + H_2O = HN_3 + HO{\cdot}CH_2{\cdot}CO{\cdot}CH_3.$$

Accordingly, it should be possible to recognise both pyroracemic aldehyde and acetol in the product, and, although we have failed to isolate these compounds, probably owing to the further action of alkali, the presence of reducing materials is indicated by vigorous action on Fehling's solution and ammoniacal silver oxide.

The Semicarbazone.—On mixing 6 grams of triazoacetone with 6·5 grams of semicarbazide hydrochloride and 5 grams of sodium acetate in water, the semicarbazone was precipitated immediately. After being recrystallised twice from absolute alcohol, it melted at 152° without evolving gas:

0·1258 gave 58·7 c.c. of nitrogen at 22° and 761 mm. N = 54·06.

$C_4H_8ON_6$ requires N = 53·84 per cent.

The semicarbazone crystallises from water or alcohol in long, brilliant needles; it effervesces with aqueous potash and, more slowly, with concentrated sulphuric acid.

This derivative has been prepared from several specimens of triazoacetone, as it forms a convenient substance by which to identify the ketone, and on one occasion the latter remained in association with excess of semicarbazide during several hours. The product in this case was quite distinct from the semicarbazone described above, being very sparingly soluble in common media, and precipitated by alkali from solution in acids. A specimen recrystallised from glacial acetic acid was therefore analysed, but the combustion presented considerable difficulty, as the substance has no definite melting point, and decomposes at a high temperature, leaving carbon:

0·1476 gave 0·1733 CO_2 and 0·0763 H_2O. C = 32·02; H = 5·78.

0·1300 „ 50·3 c.c. of nitrogen at 17° and 758 mm. N = 45·43.

$C_5H_{10}O_2N_6$ requires C = 32·25; H = 5·38; N = 45·16 per cent.

We believe therefore that this compound is the *bis-semicarbazone* of methylglyoxal,

$$CH_3{\cdot}C(:N{\cdot}NH{\cdot}CO{\cdot}NH_2){\cdot}CH:N{\cdot}NH{\cdot}CO{\cdot}NH_2,$$

because we have found that, under certain conditions, hydroxylamine is capable of transforming acetonylazoimide into methylglyoxime,

$$CH_3{\cdot}C(:NOH){\cdot}CH:NOH;$$

the latter change indicates a disposition to undergo oxidation on the part of the terminal carbon atom, recalling the behaviour of fructose towards phenylhydrazine, but, so far as we know, the alteration in question has not previously been effected by semicarbazide.

Triazoacetoxime, $N_3{\cdot}CH_2{\cdot}C(:NOH){\cdot}CH_3$.

Five grams of triazoacetone were warmed to 50° with a solution of hydroxylamine containing 4 grams of the hydrochloride in 80 c.c. of water, neutralised with 3·2 grams of anhydrous sodium carbonate; the oil dissolved, and the solution suddenly became turbid. After two hours' agitation, the product was extracted with redistilled, purified ether, and dried with sodium sulphate, the solvent being removed by exposing the liquid to a pressure of 2 mm. during four hours:

0·0786 gave 33·5 c.c. of nitrogen at 18° and 745 mm. N = 49·01.

$C_3H_6ON_4$ requires N = 49·12 per cent.

This experiment was made subsequently to an attempt to distil 50 grams of triazoacetoxime under 2 mm. pressure. On this occasion, about 25 grams boiled at 84°, whilst the residue in the flask gradually became dark brown, finally exploding with considerable violence; the distillate was colourless, and had a faint odour of prussic acid, which alone indicates decomposition, since the undistilled oxime is odourless, and, moreover, when analysed, furnished an amount of nitrogen 2 per cent. below that required by the empirical ormula $C_3H_6ON_4$. It is noteworthy that bromoacetoxime also undergoes explosive decomposition when distilled.

Triazoacetoxime is colourless, and does not solidify in the freezing mixture; its behaviour towards concentrated sulphuric acid resembles that of triazoacetic acid and ester, liberation of nitrogen occurring only after some delay, and on vigorous agitation. When treated with 40 per cent. potash, nitrogen is liberated in considerable quantities, but hydrazoic acid is also produced; if, however, more dilute alkali (20 per cent.) is employed without heating, all the nitrogen is eliminated in the form of hydrazoic acid, along with a substance having the properties of the oxime of acetol:

$$N_3\cdot CH_2\cdot C(NOH)\cdot CH_3 + H_2O = HN_3 + HO\cdot CH_2\cdot C(:NOH)\cdot CH_3.$$

Before the unstable character of triazoacetoxime was appreciated, an attempt was made to prepare this compound by the action of hydroxylamine sulphate instead of the free base. Twenty grams of triazoacetone were suspended in 300 c.c. of water, and agitated with 32 grams of hydroxylamine sulphate in 150 c.c. of water; the oil disappeared gradually but, the odour of hydrazoic acid becoming perceptible, the product was allowed to remain ten days in order to complete the change. The liquid was then extracted three times with ether, and on removing the solvent, after drying with sodium sulphate, 9 grams of a lustrous, crystalline solid separated from the oily residue; on recrystallising this product from hot benzene, of which 200 c.c. were required by 1 gram, it was found to be methylglyoxime, and was obtained in minute needles, melting at 157° without evolving gas:

0·1489 gave 35·4 c.c. of nitrogen at 18° and 756 mm. N = 27·74.
$C_3H_6O_2N_2$ requires N = 27·45 per cent.

The production of methylglyoxime and the bis-semicarbazone of methylglyoxal by the action of hydroxylamine and semicarbazide respectively on triazoacetone, is an interesting case of that type of oxidation which leads to the formation of osazones. A similar observation has been made in connexion with chloroacetoxime by Hantzsch and Wild (*Annalen*, 1896, **289**, 285) and Scholl and Matthaiopoulos (*Ber.*, 1896, **29**, 1550), methylglyoxime being obtained when excess of hydroxylamine acts on the substituted ketoxime. It is probable, also, that the same change occurs when hydroxylamine acts on hydroxyacetone, because Kling (*Ann. Chim. Phys.*, 1905, [viii], **5**, 482), who performed the experiment, records the production of a compound melting at 153°, and an analysis which furnished 26·6 per cent. of nitrogen; Kling suggests the constitutional formula,

$$CH_3\cdot C(:NOH)\cdot CH_2\cdot NH\cdot OH,$$

but, as there is no evidence for this view, it seems to us more probable that he had in hand an imperfectly purified specimen of methylglyoxime.

The p-*Toluenesulphonic Derivative.*—The oxime being an oil, it was considered desirable to characterise the substance further by preparing a crystalline derivative. Triazoacetoxime dissolved in pyridine was accordingly treated with *p*-toluenesulphonic chloride; the oil which separated on dilution with water quickly solidified, and was recrystallised from boiling light petroleum, in which the substance dissolves sparingly, 1 gram requiring about 100 c.c., from which it crystallises in large, lustrous, striated plates, melting at 73°:

0·1090 gave 20·2 c.c. of nitrogen at 23° and 757 mm. N = 21·29.

$C_{10}H_{12}O_3N_4S$ requires N = 20·90 per cent.

The substance, although snow-white when freshly crystallised, rapidly deteriorates, becoming brown in a few days. Thrown on a hot plate, it detonates, and burns with a brilliant flame; it is moderately soluble in cold methyl or ethyl alcohol, dissolving freely in chloroform, benzene, or ethyl acetate.

ROYAL COLLEGE OF SCIENCE, LONDON.
SOUTH KENSINGTON, S.W.

IX.—*The Influence of Acids and Alkalis on the Velocity of Formation of Acetoxime.*

By ERNEST BARRETT and ARTHUR LAPWORTH.

IN a paper which appeared in the July number of this Journal (Trans., 1907, **91**, 1133), it was shown by one of us that acids accelerate oxime formation, and that certain oximes are formed with great ease even in presence of concentrated hydrochloric acid. At the conclusion of the paper, a subsequent communication on measurements of the velocity of reaction between hydroxylamine and acetone and aldehyde in presence of both bases and acids was promised. The measurements referred to had been made some time before the first paper was submitted to the Society; the work had been going on for some eighteen months, and the further investigation was in progress.

In the September number of the *American Chemical Journal*, a paper by Acree and Johnson appeared (*Amer. Chem. J.*, 1907, **38**, 258), which dealt with many chapters of catalysis, and included measurements on the equilibrium point of the reversible reaction between acetaldoxime, acetone, and hydroxylamine hydrochloride, the velocity of hydrolysis of acetoxime with hydrochloric acid, and the velocity of formation of acetoxime from acetone and free hydroxylamine (*loc. cit.*, p. 308 *et seq.*).

Towards the end of November, Prof. Acree wrote stating that he had only recently seen Lapworth's paper for the first time, and drew our attention to his work with Johnson, expressing the hope that we might see our way to abandon the investigation to him. In the circumstances, we have decided to submit to the Society a brief account of the more important observations we had made before last July, when the first communication of the proposed series appeared, and the observations we select are those which appear to add something to the discoveries of Acree and Johnson and other workers, but they do not solve the question of the mechanism of the reaction. On the other hand, we have agreed to abandon the further study of the velocity of formation and hydrolysis of oximes, at least for the present, in favour of the American authors.

The work was begun some two years ago, after hearing from Stewart, the last worker on the velocity of oxime formation (Trans., 1905, **87**, 410), that he did not propose to extend his researches in this direction. The measurements were made much in the manner described by Stewart, but were carried out at 0° with solutions in which the concentrations of acetone and hydroxylamine were $N/40$ in nearly all cases. Instead of sodium phosphate, sodium acetate was used during the titrations, for it was desired to study the formation of aldoximes, in which case sodium phosphate was found to be useless.

In brief, our results supplement those of other workers in the following points. The acceleration of oxime formation by alkalis, first noticed by Auwers (*Ber.*, 1889, **22**, 605), we find to be very considerable and nearly proportional to the concentration of alkali. The acceleration of the reaction between hydroxylamine and acetone by hydrochloric acid is rather less marked at first, but rises with increasing proportions of acid very rapidly to a maximum, in which there is little or no suggestion of lag, to a point where there is present about 0·5 to 0·6 equivalent of acid, the velocity here being more than fifty times as great as with free hydroxylamine alone. It then falls almost as rapidly to the point where there is present rather more than one equivalent of hydrochloric acid, after which the variation of velocity with amount of acid present is small (see diagram, p. 92).

With acetaldehyde, more difficulty was experienced in estimating the greater velocity of reaction, and much higher dilutions were necessary. The curve obtained on plotting our preliminary results was much like that for acetone, but the point of maximum velocity was reached with a somewhat larger proportion of acid.

The acceleration of oxime formation by addition of alkali, and the approximate proportionality of the velocity to the concentration of alkali present, suggests at once that the hydroxylamine behaves as a weak acid and reacts with the carbonyl compound in much the same manner as does hydrocyanic acid (compare Trans., 1903, **83**, 997; 1904, **85**, 1214 and 1355, &c.).

Thus, to take the simplest possible ionic view, the hydroxylamine may be supposed to yield the ions $\overset{+}{H}\cdot$ and $\cdot N\overset{-}{H}\cdot OH$, the latter of which, as a weak ion, forms a complex with the carbonyl compound:

$$R_2C{=}O + \cdot\overset{-}{N}H\cdot OH \longleftrightarrow R_2\overset{-}{C}{<}\genfrac{}{}{0pt}{}{O-}{NH\cdot OH},$$

this complex ion formation being relatively very slow.

The idea that ammonia in analogous cases reacts as an acid and in the parts $\overset{+}{H}$ and $\overset{-}{NH_2}$ or $\overset{-}{NH_3}\cdot OH$ has been suggested by Knorr (*Ber.*, 1899, **32**, 731), and revived in a slightly different form by Lowry (*British Assoc. Report*, 1904, "Dynamic Isomerism," p. 11).

The question of the mechanism of the acceleration of oxime formation by acids is certainly much less straightforward. From the fact that an equilibrium is attained when acids act on acetoxime, Acree and Johnson conclude that the reaction involves the union of the hydroxylammonium ion with the ketone as neutral constituent:

$$(CH_3)_2CO + N\overset{+}{H_3}\cdot OH \longrightarrow (CH_3)_2\overset{+}{C}O\cdot NH_3\cdot OH.$$

This is highly improbable; firstly, because of the already high electro-affinity of the hydroxylammonium ion, and secondly, because all the evidence hitherto goes to show that only negative groups become attached to the carbon atom of the carbonyl group.

A more likely suggestion is that the hydroxylammonium ion is not directly concerned, but that the acetone forms complex ions with hydrogen ions which are present as the result of hydrolysis of the hydroxylamine salt:

$$(CH_3)_2CO + \overset{+}{H}\cdot \longleftrightarrow (C\overset{+}{H_3})_2C{<}^{OH}$$

(the oxonium ion $(C\overset{+}{H_3})_2C{:}O{<}^{H}$ being possibly formed at an intermediate step), and this positive ion then attacks the free hydroxylamine, forming a substituted hydroxylammonium ion:

$$(CH_3)_2\overset{+}{C}{<}^{OH} + NH_2\cdot OH \longleftrightarrow (CH_3)_2\overset{+}{C}{<}\genfrac{}{}{0pt}{}{OH}{NH_2\cdot OH}\cdot$$

Acree and Johnson's view would predict a regular rise in the velocity from the state where free hydroxylamine is present to that where there is one equivalent of acid, and after this a regular, but very slight, fall.

On the view now suggested, addition of acid to free hydroxylamine would at first produce little effect, and afterwards a rapidly increasing acceleration for a time, leading to a curve at first distinctly concave towards the line *A* in the diagram, and near and beyond the point where an equivalent of acid is present a maximum followed by a slight decreasing velocity as with Acree and Johnson's proposition.

It is not worth while at present to enlarge on these views. Neither explains the curious variation of the velocity between the points *A* and *B* on the diagram. It seems hardly possible that this can be elucidated by any view as to the mechanism of oxime formation from hydroxylamine and acetone. A supposition which would lead to a curve attaining a maximum value between these points would be one assuming that the measured change involved the interaction of free hydroxylamine, hydroxylammonium ions, and acetone, but this would be roughly of the form $y = x(a - x)$, and would show a rapid rise near *A*, a slow change near the maximum, and an increasingly rapid fall to *B*. The curve rather appears to suggest that its form may be due to a peculiarity either of acetone or of hydroxylamine itself. Is it possible, for example, that hydroxylamine gives a salt, $(NH_2 \cdot OH)_2,HCl$, yielding a base, $(NH_2 \cdot OH)_2$, by hydrolysis, and transformed by excess of hydrochloric acid into $NH_2 \cdot OH,HCl$? The tendency of the oxygenated derivatives of ammonia to form more complex aggregates may be recalled, and a salt of the formula quoted is known to be produced readily enough in the solid form, but whether this exists to any large extent as such, or as its ions, in aqueous solution, does not appear to be known. A fact which seems to militate against such an explanation is that the condition for maximum velocity with acetaldehyde does not appear to coincide with that with acetone, the point lying somewhat nearer the line *B*.

EXPERIMENTAL.

In the following series of experiments with acetone, the initial concentrations of hydroxylamine and acetone were, in all cases, *N*/40. The solutions in which the reaction was studied were prepared by mixing equal volumes of *N*/10 solution of acetone and hydroxylamine hydrochloride to the latter of which had previously been added varying quantities of sodium hydroxide or hydrochloric acid, it being so arranged that immediately after admixture there should be exactly 1 gram-molecule each of ketone and total hydroxylamine per 40 litres of solution, and all operations were carried out at 0°.

In the tables given, the amounts of hydrochloric acid or sodium hydroxide present are also stated in gram-molecules per 40 litres, and it is to be understood that the stated amount of hydrochloric acid in each case includes both the free acid and that combined with the hydroxylamine; similarly, in experiments II to IV, the amount of sodium hydroxide given refers to the excess of the latter used over that required to convert all the hydroxylamine present into free base. In the majority of the experiments, therefore, sodium chloride was necessarily present, but we have found that the effect of this salt was hardly perceptible, and did not produce any effect on the velocity of reaction sufficient to alter in any way the general conclusions to which the investigation leads.

After many preliminary trials, the method adopted for estimating the amount of oxime formed was to determine the quantity of hydroxylamine which remained by oxidising it with excess of standard iodine solution as other workers have done, but having found that in alkaline media, such as sodium phosphate or bicarbonate, concordant results could not be obtained in presenee of aldehydes, we were finally led to carry out the titrations in presence of sodium acetate. This salt, if highly purified, serves a similar purpose, and in its presence hydroxylamine may be determined with a very fair degree of accuracy, providing that much free acid is not present with the hydroxylamine.

In each case, the time which elapsed between the moment of admixture and that of withdrawing an aliquot portion of the solution for titration is given in minutes. The number indicating the amount of oxime formed represents the number of gram-molecules present per 4000 litres, the maximum possible at the end point being, of course, equal to 100, and was arrived at by subtracting the quantity of hydroxylamine unchanged in 40 litres from 100. The last number in each case represents the quantity of oxime formed at the end point.

I. No acid or alkali present (that is, the solution was prepared so as to contain 1 gram-molecule each of hydroxylamine, hydrochloride, and acetone per 40 litres, the free base being liberated by addition of 1 gram-molecule of sodium hydroxide per 40 litres):

$t=$	2	5	10	20	30	—
Oxime formed =	5·8	17·0	29·2	43·7	52·9	99·5

SERIES 1.—*In Presence of Alkali.*

II. 0·20 gram-molecule of free sodium hydroxide present. In experiments II to IV a quantity of acid sufficient to neutralise the alkali present was added to the sodium acetate before the titration of hydroxylamine:

t=	2	5	10	21	36	—
Oxime formed=	33·9	52·2	69·6	83·0	89·3	99·5

III. 0·25 gram-molecule of sodium hydroxide present:

t=	2	5	10	20	—
Oxime formed=	49·5	68·3	81·6	90·9	98·8

IV. 1·00 gram-molecule of sodium hydroxide present:

t=	1	2	5	10	20	—
(*a*) Oxime formed=	—	64·3	82·7	92·3	97·1	100
(*b*) ,, ,, =	51·4	66·3	84·4	92·6	97·9	00

SERIES 2.—*In Presence of Acid.*

V. 0·066 gram-molecule of hydrogen chloride present:

t=	3	5	10	20	30	—
Oxime formed=	7·3	13·4	28·7	52·2	68·6	98·1

VI. 0·25 gram-molecule of hydrogen chloride present:

t=	2	5	10	20	30	—
Oxime formed=	19·3	43·9	73·8	81·7	83·5	85·9

VII. 0·30 gram-molecule of hydrogen chloride present:

t=	1	2	5	10	15	—
Oxime formed=	21·7	34·5	67·4	81·4	85·0	85·8

VIII. 0·40 gram-molecule of hydrogen chloride present:

t=	1	2	5	11	20	—
Oxime formed=	19·1	38·0	64·7	72·6	77·6	77·6

IX. 0·50 gram-molecule of hydrogen chloride present:

t=	2	5	10	20	30	—
Oxime formed=	49·8	54·5	65·2	68·9	70·4	71·0

X. 0·60 gram-molecule of hydrogen chloride present:

t=	1	2	5	18	25	36	—
Oxime formed=	31·6	44·2	54·9	68·5	68·5	69·4	69·4

XI. 0·75 gram-molecule of hydrogen chloride present:

t=	2	5	10	20	30	—
Oxime formed=	31·3	46·5	50·4	58·7	61·1	61·9

XII. 1·00 gram-molecules of hydrogen chloride present (that is to say, in this experiment, initially only acetone and hydroxylamine hydrochloride were present):

t=	2	5	10	15	37	—
Oxime formed=	16·3	28·6	40·1	46·1	57·1	60·5

XIII. 1·50 gram-molecules of hydrogen chloride present:

$t=$	2	5	10	20	35	—
Oxime formed =	3·6	7·7	21·5	32·1	45·1	58·3

XIV. 1·512 gram-molecules of hydrogen chloride present:

$t=$	1	2	5	10	25	—
Oxime formed =	1·6	4·7	12·6	23·5	32·7	58·3

XV. 1·64 gram-molecules of hydrogen chloride present:

$t=$	2	5	10	20	30	—
Oxime formed =	4·1	13·4	18·5	28·0	35·3	55·0

XVI. 2·024 gram-molecules of hydrogen chloride present:

$t=$	1	2	5	11	25	—
Oxime formed =	1·6	2·0 (?)	12·2	23·8	31·2	50·6

In the last cited and in other experiments in which more than 2 molecular proportions of acid were present, the disturbing influence of the excess of acid on the titration of the hydroxylamine makes itself felt. In all cases, the quantity of hydroxylamine found was greater than that really present, so that the amount of oxime calculated on the same basis as in the preceding experiments appears less than is actually the case. Nevertheless, the results showed clearly enough that, even when as much as 40 molecular proportions of hydrogen chloride are present, oxime formation takes place with considerable velocity, and this does not appear to vary much within very wide limits. It had been our intention to examine this region, using sodium phosphate instead of acetate as the medium during titration.

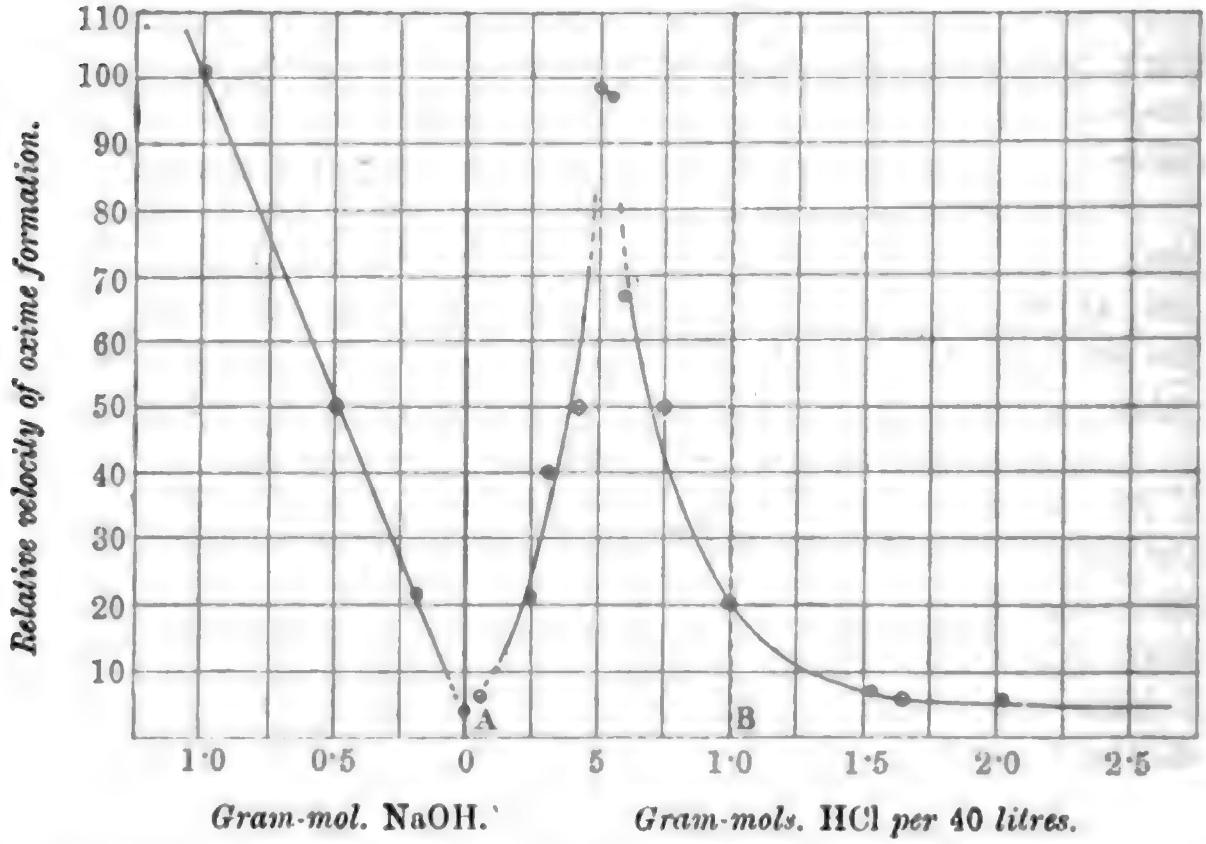
Fairly concordant numbers obtained on repeating a considerable number of the above experiments, indicate that the results may be regarded as correct within 2—3 units.

We have also carried out experiments on similar lines, using acids other than hydrochloric acid, but the results were without much further significance.

The most noteworthy points revealed by a glance at the numbers in the above tables are, first, that there is a minimum velocity at, or very near, the point where only acetone and hydroxylamine are present (experiment I); secondly, that very large acceleration is caused by the addition of alkalis or acids, the former having proportionately a considerably greater influence; thirdly, that there is a maximum velocity point between this point and that where the solution contains nothing but acetone and hydroxylamine hydrochloride. This is at about the point attained in experiment IX, and, as will be seen, the amount of oxime formed here in two minutes is larger than in any other case on the side where acid is present; fourthly, beyond this point rapid fall in the velocity occurs, but even where an enormous excess of acid is present there is evidence that the velocity of oxime formation remains perhaps larger than when free hydroxylamine alone is present.

Owing to the rapid change of the velocity with acidity (and this varies during each experiment), it is not possible to obtain velocity constants, and the errors of time measurement in the first stages of the oxime formation render it difficult to obtain a value for the initial velocity under any prescribed conditions. However, remembering that when much acid is present partial hydrolysis of the oxime occurs, the reaction therefore being incomplete, a fair idea of the relative velocities with different conditions as to concentration of acid and alkali may be obtained by carefully plotting the results and ascertaining the time required for the reaction to proceed half way to the point at which change ceases. It is clear, of course, that it would be better to take points corresponding to one-quarter, one-tenth, or less, but this leads to a magnification of other errors, and it may be stated that the curves thus obtained are found to be very similar, showing precisely the some peculiarities.

The following diagram exhibits the velocity of reaction estimated by taking the inverse of the time required for the reaction to proceed half-way towards completion. The vertical line at A corresponds with conditions when acetone and free hydroxylamine only are present; to the left of this, alkali, and, to the right, acid is present. The vertical line at B corresponds with the point where acetone and hydroxylamine hydrochloride only are present.



The velocities were found by ascertaining, graphically, the time required for the formation of one-half the amount of oxime present at equilibrium point, and the numbers given are one hundred times the reciprocals of these.

The method of exhibiting the results, although rough, at least affords a general idea of some of the peculiarities in the formation of acetoxime. It is difficult to state precisely the points or magnitudes of the maximum or minimum velocities, but greater or less deviations than those indicated have not been found in spite of repeated search with slightly varying conditions.

It is noteworthy that the extension of the curve on the right appears to be nearly horizontal beyond the limits shown; in other words, it seems that with excess of hydrochloric acid the velocity varies only very slightly with the concentration.

By varying either the amount of acetone or hydroxylamine while keeping the concentration of the other unaltered, we have ascertained that the velocity is nearly proportional to the concentration of each of these separately.

The nature of the results we obtained in using acetaldehyde instead of acetone have already been alluded to. We hesitate to give the details, because those experiments were of a preliminary character, and, owing to the much higher dilution necessary, subject to errors which we hoped to be able to eliminate on repeating the measurements.

Our thanks are due to the Research Fund Committee of the Chemical Society for a grant, which helped to defray the cost of the investigation.

GOLDSMITHS' COLLEGE, NEW CROSS, S.E.

X.—*A Colorimetric Method for the Determination of Small Percentages of Iron in Copper Alloys.*

By ARNOLD WILLIAM GREGORY, B.Sc. (Lond.).

IT is often a matter of considerable importance to be able to determine accurately the amount of iron in copper alloys, on account of the effect of this element on their physical properties. The gravimetric methods are such that only by working with very large quantities of material can accurate results be obtained. Moreover, there is always a danger of iron being introduced into the solution of the alloy by the addition of large quantities of reagents which may contain a trace of that element, and from external sources during the lengthy method of procedure.

The following method has been found to give extremely accurate results; it is simple in operation, and very rapid in execution. It is based upon the colour reaction given by salicylic acid and ferric chloride. The violet coloration produced when salicylic acid is added to ferric chloride, although affording a delicate test for iron under properly chosen conditions, cannot be relied on for the quantitative determination of that element, since the colour is destroyed in the presence of mineral acids and also by excess of alkalis.

If, however, an excess of a solution of sodium acetate be added to a ferric salt, and then a solution of salicylic acid in acetic acid, a deep red colour is produced. Under these conditions, the depth of colour is proportional to the amount of iron present, and this method may be used for the estimation of small quantities of iron.

In the case of copper alloys, the blue or green colour of the solution entirely masks the red colour produced by the iron. This difficulty is overcome by the addition of a weak solution of potassium cyanide in quantity sufficient for the formation of the colourless, complex cyanide of copper and potassium. The red colour is unchanged by this treatment. The exact method of procedure is as follows: 0·2 gram of the alloy is dissolved in a minimum quantity of strong nitric acid. If a precipitate is produced, due to tin or antimony, the liquid is diluted slightly and filtered. Lead, if present, must be removed as sulphate.

To this solution, 20 c.c. of a concentrated solution of sodium acetate are added, and 10 c.c. of a 2 per cent. solution of salicylic acid in glacial acetic acid. A 3 per cent. solution of potassium cyanide is now added gradually until the green colour of the solution has disappeared, and the precipitate of copper cyanide is re-dissolved. The solution, which is red if iron is present, is now made up to a definite volume (depending on the intensity of the colour), and a measured amount is transferred to a Nessler comparison tube.

Into a similar tube, 20 c.c. of sodium acetate solution and 10 c.c. of the salicylic acid solution are placed, and diluted to approximately the same volume as the solution of the alloy. A standard solution of ferric chloride is added drop by drop, with constant stirring, until the colour produced is similar in intensity in the two tubes. From the amount of the standard solution used, the percentage of iron may be calculated.

By this method, it is possible to detect as little as 0·00002 gram of iron in the presence of 0·2 gram of copper.

A strong solution of potassium cyanide must on no account be used, as this gives a coloured solution with pure copper salts, especially on warming.

This test cannot be satisfactorily employed in the case of alloys containing considerable percentages of bismuth. Zinc and antimony, however, may be present without any appreciable error being introduced.

EXPERIMENTAL.

A solution of pure copper sulphate was made, such that 1 c.c. was equivalent to 0·02 gram of copper. Ten c.c. of this solution and 3 c.c. of concentrated nitric acid were placed in each of seven beakers, and to all but the first of these varying amounts of a standard solution of ferric chloride were added. The tests were then carried out as described above, the solutions in each case being made up to 100 c.c. The results obtained are given in the following table. The second column shows the number of c.c. of ferric chloride solution added to the copper sulphate; the third gives the percentage of iron that each quantity represents; the fourth gives the number of c.c. of ferric chloride required to produce the same colour as that obtained in each of the test experiments, and the fifth shows the percentage of iron calculated from the volume of ferric chloride added:

Number.	C.c. of $FeCl_3$ used.	Per cent. Fe.	C.c. of $FeCl_3$ required.	Per cent. Fe
1.	nil	nil	nil	nil
2.	1	0·01	1·1	0·011
3.	2	0·02	2·1	0·021
4.	5	0·05	5·2	0·052
5.	10	0·10	10·4	0·104
6.	15	0·15	15·7	0·157
7.	20	0·20	21·0	0·210

APPLEBY IRON WORKS,
FRODINGHAM.

XI.—*Derivatives of Tetramethyl Glucose.*

By JAMES COLQUHOUN IRVINE, D.Sc., Ph.D., and AGNES MARION MOODIE, M.A., B.Sc. (Carnegie Scholar).

IN previous study of alkylated sugars attention has been chiefly directed to reactions in which derivatives of a glucosidic nature are produced, and such compounds have been found to show, in general, a close relationship with the corresponding derivatives of the parent unalkylated sugars. In the present investigation, we have extended our work on tetramethyl glucose with the view of ascertaining whether the analogy also holds for derivatives generally regarded as non-glucosidic.

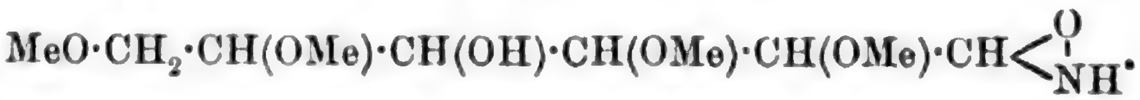
Our results show that tetramethyl glucose enters into all the characteristic reactions of the parent sugar, and, moreover, the optical rotations of the products are on the whole comparable with those of the corresponding unalkylated compounds. Several irregularities were observed, but apparently methylation has little effect on the characteristic chemical reactions of reducing sugars, except in increasing the stability of the compounds. In the first place, we have studied reactions in which the alkylated sugar might be expected to react as an alkyloxy-aldehyde, giving products in which the γ-oxidic linking, characteristic of reducing sugars and glucosides, should be absent. In the case of dextrose, the only simple condensation compounds which are regarded as derived from a hydroxy-aldehyde are the acetals, mercaptals, hydrazones, oxime, and anilide. This view of the constitution of the last compound has, however, not escaped criticism, and many arguments support the γ-oxidic structure (*Ber.*, 1894, **27**, 1287).

We find that in the case of tetramethyl glucose, there seems no reasonable doubt that both the oxime and anilide do possess the γ-oxidic linking in the sugar residue, and are thus to be regarded as derived from the α- or β-form of the sugar and not from the aldehydic isomeride. With regard to the tetramethyl glucosephenylhydrazone, our conclusions are unfortunately not supported by analytical data, but the structure of the compound seems to differ essentially from that of the anilide or oxime, and may possibly thus belong to the aldehydic type.

Tetramethyl glucoseoxime was readily prepared by the action of hydroxylamine on a methyl-alcoholic solution of the sugar. Even after repeated fractional crystallisation, the melting point was indefinite (61—68°), suggesting that the specimen was a mixture of stereoisomeric forms. The compound differed from glucoseoxime in that no indication of mutarotation could be detected, either in alcoholic or aqueous solutions. The specific rotation in methyl alcohol was $[\alpha]_D^{20}$ + 25·9°, a result which is comparable with the marked diminution in rotatory power observed when glucose is converted into its oxime. The constitution of the compound admits of several possibilities. Accepting the normal oxime structure, we have:

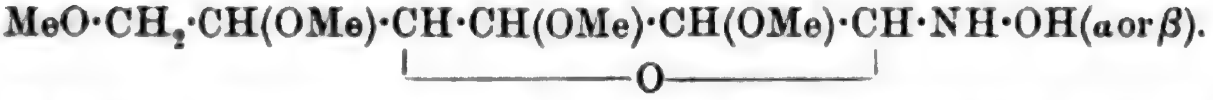
I. $MeO\cdot CH_2\cdot CH(OMe)\cdot CH(OH)\cdot CH(OMe)\cdot CH(OMe)\cdot CH{:}NOH$,

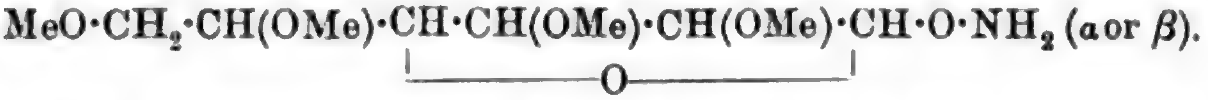
which might exist in *syn-* and *anti*-modifications. As an alternative, the following structure is possible:

II. 

$$MeO\cdot CH_2\cdot CH(OMe)\cdot CH(OH)\cdot CH(OMe)\cdot CH(OMe)\cdot CH{<}\begin{matrix}O\\ |\\ NH\end{matrix}.$$

On the other hand, if the sugar reacts in the γ-oxidic form, the condensation may give rise to four isomerides:

III. 
$MeO\cdot CH_2\cdot CH(OMe)\cdot \underbrace{CH\cdot CH(OMe)\cdot CH(OMe)\cdot CH}_{O}\cdot NH\cdot OH$ (α or β).

IV. 
$MeO\cdot CH_2\cdot CH(OMe)\cdot \underbrace{CH\cdot CH(OMe)\cdot CH(OMe)\cdot CH}_{O}\cdot O\cdot NH_2$ (α or β).

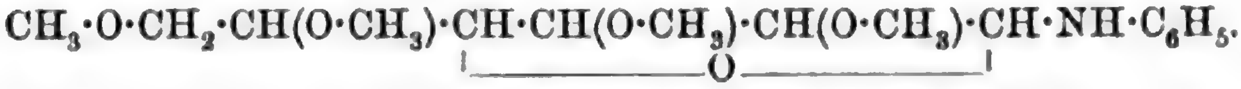
Of these possibilities, formula I alone represents a true oxime, and formula IV a true glucoside, as only in the latter case is the sugar molecule linked to the remaining group through an oxygen atom. The effect of alkylation on the compound offers a ready solution of the problem of its constitution. In the event of formulæ I or II being correct, methylation should introduce two methyl groups, and hydrolysis of the product should give aldehydic pentamethyl glucose. In the case of formula III, only one alkyloxy-group could enter the molecule, and tetramethyl glucose should be formed on hydrolysis of the product. On the other hand, formula IV represents a compound in which the methoxyl content could not be increased.

We find that by applying the silver oxide reaction to tetramethyl glucoseoxime, a derivative is formed containing five methoxyl groups, and, on hydrolysis, tetramethyl glucose is regenerated in almost quantitative amount. This result at once disposes of formulæ I, II, and IV. The absence of mutarotation may thus be explained, as, whatever the cause of this phenomenon in oximes may be, it is presumably dependent on the presence of the double bond.

Evidence was also obtained that our preparation of tetramethyl glucoseoxime consisted of two stereoisomeric forms, as, during hydrolysis, the specific rotation at first diminished very rapidly, and afterwards increased steadily to a constant value. Previous experience in the hydrolysis of alkyl glucosides has shown that this behaviour is significant of the presence of two stereoisomerides, which differ widely in their rotatory powers and rates of hydrolysis. Moreover, a similar result was observed during the hydrolysis of the pentamethylated oxime, which was doubtless also a mixture of α- and β-forms. It might be mentioned here that the latter hydrolysis showed many features in common with that of the natural glucoside, gynocardin, described by Power and Lees (Trans., 1905, **87**, 355). Contrary to expectation, the process was extremely slow, prolonged boiling with hydrogen chloride being necessary, and hydrogen cyanide was steadily evolved for some hours.

Before arriving at the above conclusion as to the constitution of tetramethyl glucoseoxime, we took the precaution of subjecting various other oximes to the joint action of silver oxide and methyl iodide. The substances selected for experiment were chosen with a view to testing the effect of the process on widely different types of oximes. In each case, the methylation proceeded normally, giving fully alkylated derivatives. Thus œnanthaldoxime was readily converted into a monomethyl ether, whilst salicylaldoxime and benzoinoxime gave the corresponding dimethyl ethers. This shows that the oximido-group, in common with any other hydroxyl group which may be present, is capable of ready methylation by the silver oxide method, and the results arrived at by this process are therefore valid in deducing the constitution of oximes. The method, moreover, possesses many obvious advantages in the determination of the hydroxyl content of oximes, as the use of acetic anhydride in such estimations frequently results in molecular rupture or in nitrile formation, and, in addition, the products are often difficult to purify.

Our examination of tetramethyl glucoseanilide has led to a similar conclusion as to its constitution. The compound, which was prepared by boiling an alcoholic solution of the sugar and the base, crystallised in long needles, melting at 132—134°. In acetone solution, it showed a high dextrorotation ($[\alpha]_D^{20}$ +229·5°), and no mutarotation was observed. Apparently only one form was present in this crystalline specimen, as during hydrolysis the specific rotation decreased continuously without fluctuation. The compound was quite unaltered after several successive treatments with silver oxide and methyl iodide, and, as in no previous case has any soluble hydroxy-compound resisted the action of these reagents, we conclude that the anilide is a γ-oxidic form, and possesses the following formula:



$$CH_3\cdot O\cdot CH_2\cdot CH(O\cdot CH_3)\cdot \underbrace{CH\cdot CH(O\cdot CH_3)\cdot CH(O\cdot CH_3)\cdot CH}_{O}\cdot NH\cdot C_6H_5.$$

Experiments are at present in progress, in which the constitution of glucoseanilide is being further investigated.

The results obtained on applying similar methods to tetramethyl glucosephenylhydrazone were not so conclusive. The product of the methylation failed to crystallise, and could not be distilled under diminished pressure on account of decomposition. On hydrolysis, however, in addition to aniline and methylaniline, a colourless dextrorotatory syrup was obtained, which did not affect Fehling's solution; it therefore contained no tetramethyl glucose. As the substance was easily resinified, we were unable to identify it definitely as pentamethyl glucose, although its reactions agreed with those which might be expected for such a compound. At all events, the absence of tetramethyl glucose in the hydrolysis products points to the conclusion that the hydrazone of tetramethyl glucose differs essentially in structure from the corresponding oxime and anilide.

The halogen derivatives of tetramethyl glucose, obtained by the action of phosphorus halides on the sugar, show considerable chemical similarity to those obtained from tetra-acetyl glucose. Both tetramethyl chloroglucose and tetramethyl bromoglucose are uncrystallisable syrups, the latter being very unstable. Both compounds are decomposed by water, and react with methyl alcohol in presence of silver carbonate to give a mixture of the α- and β-tetramethyl methylglucosides, a result which indicates that the preparations are also mixtures of α- and β-forms. Judging from the relative proportions of the two glucosides thus formed, and using this as an index of the composition of our preparation of tetramethyl chloroglucose, more than 70 per cent. of the β-form must have been present. The bromoderivative, like tetra-acetyl bromoglucose, could only be preserved for a few days without spontaneous decomposition. It was found that the substance could be applied synthetically in the formation of other alkylated glucosides. When dissolved, along with the molecular proportion of benzoin, in acetone and the solution heated with silver oxide, benzoin tetramethylglucoside, melting at 105—106°, was produced. This change, in which the alkylated sugar residue is introduced into the hydroxyl position, may be regarded as a modification of the silver oxide reaction.

We have also studied the action of a methyl-alcoholic solution of hydrogen chloride on tetramethyl glucose with the object of determining if the condensation of the alcohol and the sugar depends on the intermediate formation of an acetal compound. In previous cases (Trans., 1904, **85**, 1063), this reaction has been conducted at 40°, using invariably 0·25 per cent. of hydrogen chloride, but in the present instance the effect of different concentrations of the acid at 20° was ascertained polarimetrically. Using a methyl-alcoholic solution containing 5 per cent. of the sugar and 8 per cent. of hydrogen chloride, the specific rotation diminished very rapidly, but without fluctuation. The total optical change, which was complete in one hour, was α_D $+79·2° \longrightarrow +69·1°$. It will be seen that the initial rotation observed is lower than that found for tetramethyl glucose; this is doubtless due to the very rapid condensing action of the acid. The product consisted as usual of a mixture of the isomeric tetramethyl methylglucosides, and no indication of acetal formation was observed. A similar result was obtained by the substitution of 0·25 per cent. acid. In this case, the condensation was very slow at 20°, but the specific rotation of the solution, which was initially +84·8°, decreased steadily and ultimately became constant at +70·1°. The use of 0·1 per cent. acid naturally occasioned very slow reaction, but in this case the change of specific rotation was not regular. During the first twenty-four hours, a fall of 9° in $[\alpha]_D$ was observed; this was followed by a slow increase, occupying seventeen hours, to nearly the initial value. Thereafter the rotation diminished very slowly indeed, and the constant value, $[\alpha]_D$ +66·8°, was only reached after the lapse of seven months. These optical changes cannot be ascribed to mutarotation of the sugar, or to the interconversion of the alkylated glucosides (Trans., 1904, **85**, 1068; 1905, **87**, 905), but, nevertheless, on examining samples of the solution at intervals, nothing was isolated from the product except the alkylated glucosides, mixed, when the condensation was incomplete, with quantities of unaltered tetramethyl glucose. This reaction therefore gives no indication of the sugar reacting in the aldehydic form.

The ready solubility of alkylated sugars in organic solvents enabled us to apply the Grignard reaction to tetramethyl glucose. This reaction has already been successfully carried out on tetra-acetyl-*d*-gluconolactone by Paal and Hörnstein (*Ber.*, 1906, **39**, 1361), who obtained αβγδεζ-hexahydroxy-αα-diphenylhexane as the main product. In our experiments, however, using magnesium methyl iodide, we have only obtained negative results so far, the alkylated sugar being recovered unaltered.

It will thus be seen that with the exception of the doubtful case of tetramethyl glucosehydrazone, all the derivatives so far obtained from tetramethyl glucose belong to the γ-oxidic type.

EXPERIMENTAL.

Preparation of Tetramethyl Glucoseoxime.

Ten grams of the alkylated sugar were dissolved in methyl alcohol (200 c.c.) containing slightly more than one molecular proportion of hydroxylamine, and the solution was boiled for 90 minutes under a reflux condenser. The alcohol was then evaporated, the crystalline residue dissolved in dry ether, and the solution filtered. On evaporation of the solvent, a colourless syrup remained, which rapidly solidified to a mass of slender, prismatic needles; these were drained from adherent oil on a porous plate. The finely-powdered substance was afterwards extracted repeatedly with boiling light petroleum in order to remove traces of unaltered tetramethyl glucose, and then recrystallised from a mixture of equal parts of light petroleum and anhydrous ether. When microscopically examined, the crystals appeared homogeneous, and, moreover, the specific rotations of successive crops were practically constant, but, nevertheless, after repeated crystallisation the melting point was rather indefinite (61—68°). Analysis gave:

$C = 47.51$; $H = 8.44$; $CH_3 \cdot O = 48.6$; $N = 6.01$.

$C_6H_9O_2N(O \cdot CH_3)_4$ requires $C = 47.81$; $H = 8.36$; $CH_3 \cdot O = 49.4$; $N = 5.58$ per cent.

Tetramethyl glucoseoxime is readily soluble in water and all organic solvents with the exception of light petroleum, and the aqueous solution has no action on Fehling's solution in the cold, but effects vigorous reduction on boiling. A 5 per cent. solution in methyl alcohol showed a specific rotation of +25·9°, which remained unaltered after twenty-four hours. A similar solution in water gave $[\alpha]_D^{20}$ +27·8°, and here, also, no evidence of mutarotation was observed even after several days.

The hydrolysis of the oxime was effected by heating with excess of 8 per cent. aqueous hydrogen chloride at 100°. The hydrolysis, however, commenced even at the ordinary temperature, as, on standing, the value for $[\alpha]_D$ was found to decrease from +27·8° to +15·0°. On now heating to 100°, the dextrorotation rapidly increased, and after fifty minutes' treatment remained constant. The value then obtained, if calculated on the basis that tetramethyl glucose was the only active product of the hydrolysis, was +83·7°, a number which agrees very closely with the constant specific rotation of the alkylated sugar in water. The solution was neutralised with barium carbonate, evaporated to dryness, and the residue extracted first with ether and afterwards with a mixture of alcohol and ether. The former extract gave tetramethyl glucose (m. p. 84—85°), and the latter hydroxylamine hydrochloride, and these substances constituted the sole products of the hydrolysis.

Alkylation of Tetramethyl Glucoseoxime.

On adding silver oxide (5 mols.) to tetramethyl glucoseoxime (1 mol.) dissolved in methyl iodide (10 mols.), a vigorous, spontaneous reaction ensued, which was completed by heating on a water-bath for three hours. The product was extracted with boiling ether, and, on evaporation of the solvent, a clear, yellow, neutral liquid was obtained. After a second alkylation in which the same proportions of alkylating mixture were used, the compound was fractionated under diminished pressure (b. p. 144—146° under 10 mm. pressure). Analysis gave:

$C = 49·98$; $H = 8·60$; $CH_3·O = 57·13$; $N = 5·56$.

$C_{11}H_{23}O_6N$ requires $C = 49·81$; $H = 8·68$; $CH_3·O = 58·49$; $N = 5·28$ per cent.

The analyses not only indicate that only one methoxyl group had been introduced, but exclude the possibility of the presence of pentamethyl glucon準nitrile.

The alkylated oxime is a colourless, neutral, mobile liquid, soluble in all ordinary solvents, and possessing no action on Fehling's solution except on prolonged boiling. The optical activity of different preparations was almost constant, a five per cent. solution in methyl alcohol giving $[\alpha]_D^{20}$ +39·8° without mutarotation.

Hydrolysis of Tetramethyl Glucoseoxime Methyl Ether.

The hydrolysis of the alkylated oxime presented considerable difficulty. A 4 per cent. solution of the compound was prepared in water containing 5 per cent. of hydrogen chloride, and heated in boiling water. As in the case of the parent oxime, the dextro specific rotation at first diminished from 38·1° to 29·8°, and afterwards steadily increased, during three hours' treatment, to the value +50°. During the reaction, appreciable quantities of hydrogen cyanide were evolved, and, judging by the increase in specific rotatory power, the hydrolysis proceeded only slowly at 100°. Accordingly, the liquid was maintained at the boiling point, the evolved hydrogen cyanide being removed in a current of air. After six hours' treatment, the evolution of the gas ceased; the solution was neutralised with barium carbonate and worked up as usual. A nearly quantitative yield of tetramethyl glucose, melting after recrystallisation at 84° and showing the specific rotation, $[\alpha_D^{20}]$ +87·8°, was obtained as the product of the hydrolysis.

Alkylation of Different Types of Oximes.

The methylation of these oximes was carried out for the purposes explained in the introduction.

Alkylation of Œnanthaldoxime.—This substance was selected for experiment as a type of compound containing one hydroxyl group directly linked to the nitrogen atom. The oxime was readily soluble in methyl iodide, and was alkylated as usual by the joint action of the alkyl halide and dry silver oxide. After two treatments, the product was fractionated under reduced pressure, and obtained as a colourless liquid boiling at 65—66° under 15 mm. pressure.

Analysis pointed to the fact that methylation had proceeded normally:

Found, C = 66·86; H = 11·71; $CH_3 \cdot O$ = 19·50.

$C_7H_{14}N \cdot O \cdot CH_3$ requires C = 67·13; H = 11·88; $CH_3 \cdot O$ = 21·68 per cent.

Alkylation of Salicylaldoxime.—In the case of salicylaldoxime, the reaction with silver oxide and methyl iodide was very vigorous. The product was a mobile liquid, which was distilled at 125—127°, under 16 mm. pressure. As the compound burned with explosive violence, ordinary combustions could not be undertaken, but a Zeisel estimation gave $CH_3 \cdot O$ = 37·11, the calculated value, assuming that two methoxyl groups had entered the molecule, being 37·57 per cent. The constitution of the compound was also proved by the formation of salicylaldehyde methyl ether during hydrolysis. As the melting point of the latter compound shows considerable variation, the product of the hydrolysis was identified by conversion into *o*-dimethoxybenzoin (Trans., 1901, 79, 670), melting at 101·5°. This result shows that both the phenolic and oximido-groups present in the oxime had undergone normal alkylation.

Alkylation of Benzoinoxime.—In this case, two successive alkylations were found to be necessary, as the oxime did not dissolve readily in the alkyl iodide, and consequently the addition of acetone was necessary in the first treatment with the methylating agents. The product was obtained as a colourless oil boiling at 182—184° under 16 mm. pressure. Analysis gave:

C = 74·94; H = 6·85; N = 5·66.

$C_{14}H_{11}N(O{\cdot}CH_3)_2$ requires C = 75·29; H = 6·66; N = 5·47 per cent.

As the compound resinified with hydrogen iodide, the results of the methoxyl determinations were invariably low (found, $CH_3{\cdot}O = 18{\cdot}22$, calculated for two methoxyl groups, $CH_3{\cdot}O = 24{\cdot}31$ per cent.). The presence of a methoxyl group in the benzoin side-chain was, however, confirmed by hydrolysis. This was effected by boiling in aqueous alcoholic solution containing 8 per cent. of hydrogen chloride. After two hours' treatment, the product was precipitated with water and extracted with ether. The ethereal extract, after treatment with sodium carbonate, yielded on evaporation a crystalline product which, after recrystallisation from light petroleum, melted at 49—51°, and was therefore identified as benzoin methyl ether.

Tetramethyl Glucoseanilide.

On boiling an alcoholic solution of equimolecular proportions of the sugar and aniline for several hours, partial condensation took place with the formation of tetramethyl glucoseanilide. The yield of the latter was, however, materially increased by using a considerable excess of the base. Equal weights of tetramethyl glucose and aniline were dissolved in the minimum quantity of absolute alcohol, and the solution was boiled for four hours. As the crude anilide darkened rapidly when heated to 100°, the removal of the solvent alcohol and excess of aniline was effected by heating to 60° under reduced pressure. The semi-crystalline residue was drained on a porous tile, washed with cold water to remove traces of the sugar, and recrystallised twice from anhydrous ether. Analysis gave:

C = 61·50; H = 8·18; $CH_3{\cdot}O = 40{\cdot}49$.

$C_{16}H_{25}O_5N$ requires C = 61·74; H = 8·04; $CH_3{\cdot}O = 39{\cdot}87$ per cent.

The *anilide* crystallises from ether in long needles, melting sharply at 135°, and is apparently homogeneous. It is readily soluble in organic solvents, but is practically insoluble in water. When boiled for a considerable time with water, the substance is partly hydrolysed. The specific rotation of a 3 per cent. solution in acetone was $[\alpha]_D^{20}$ +229·5°, and no mutarotation was detected even after adding a trace of alcoholic ammonia. The compound was hydrolysed by mixing an acetone solution with an equal volume of 10 per cent. hydrogen chloride and heating to 50°. The dextrorotation diminished steadily without fluctuation, and, on working up the products, tetramethyl glucose and aniline were isolated.

Attempted Alkylation of Tetramethyl Glucosideanilide.

The methylation of the compound was attempted in order to determine whether the anilide is a condensation derivative of the sugar in its aldehydic or γ-oxidic form. A solution of the compound (1 mol.) in methyl iodide (10 mols.) was heated on a water-bath with silver oxide (5 mols.). There was no apparent reaction, and on working up the product after several hours' treatment the original weight of anilide was recovered unaltered in melting point and specific rotation. A second alkylation was tried, in which heating with a large excess of the alkylating mixture was continued for three days, but with a similar result. Additional evidence that no alkylation had occurred was furnished by the fact that only 8 per cent. of the silver oxide was converted into iodide. As in no previous case has any hydroxy-compound resisted this treatment, we conclude that the anilide is a γ-oxidic form.

Alkylation of Tetramethyl Glucosephenylhydrazone.

The hydrazone was prepared as already described (Trans., 1903, **83**, 1033), and alkylated in the usual manner. The crude product, which was a bright red syrup insoluble in water or light petroleum, but readily soluble in organic solvents generally, could not be obtained in a crystalline state. The syrup gave in methyl-alcoholic solution $[\alpha]_D^{20}$ +24·7°, a value which does not differ notably from the rotatory power of the parent hydrazone ($[\alpha]_D^{20}$ +16·6°). When heated under reduced pressure, the compound decomposed; even on standing at the ordinary temperature, the red colour became much darker, and accordingly no analyses were attempted. The hydrolysis of the product of alkylation was, however, undertaken in the hope of gaining information as to the probable constitution of the compound. When boiled for ten hours with aqueous methyl alcohol containing 4 per cent. of hydrogen chloride, no appreciable change occurred, and consequently the acid was replaced by very dilute aqueous sodium hydroxide, which has no appreciable action on tetramethyl glucose. On now heating on a water-bath, a quantity of gas was disengaged, which was absorbed in hydrochloric acid, the solution giving the test for a primary amine. The mixture was then distilled with steam, and the volatile oils were converted into the hydrochlorides and treated with nitrous acid. The oily precipitate thus formed was extracted with ether, the solvent evaporated, and the residual oil mixed with concentrated sulphuric acid. The formation of a dark blue colour showed the joint presence of phenol and nitrosoamine, proving that both aniline and methylaniline must have been produced in the hydrolysis. The aqueous product of the hydrolysis was neutralised and worked up as usual. In this way, a colourless, uncrystallisable, neutral syrup was obtained, which had no action on Fehling's solution even after heating with acids. In alcoholic solution, the substance was strongly dextrorotatory. The compound, which became resinous on standing, could not be obtained in a pure form, and consequently was not further examined, but its behaviour agrees approximately with the probable reactions of pentamethyl glucose in its aldehydic form. The combined results of the hydrolysis therefore point to the conclusion that alkylation of the hydrazone leads to the introduction of two methyl groups, one in the γ-position in the sugar-chain, and the other in the phenylhydrazine residue. This result differs sharply from those obtained in the case of the oxime or anilide, where the sugar residue in the molecule was not affected by further alkylation.

Halogen Derivatives of Tetramethyl Glucose.

Tetramethyl chloroglucose was prepared by heating a 10 per cent. solution of the sugar in benzene with the molecular proportion of phosphorus pentachloride. The reaction was carried out on a water-bath, and was continued for thirty minutes. The benzene was then removed under diminished pressure, the residue dissolved in ether, and shaken repeatedly with water. The ethereal extract was dried over anhydrous sodium sulphate, and shaken successively with barium carbonate and silver carbonate. On evaporation of the solvent, a colourless oil remained, soluble in organic solvents, but insoluble in cold water. When warmed with water, the oil passed readily into solution with the formation of tetramethyl glucose and hydrogen chloride. The substance, which was free from phosphorus compounds, was completely decomposed on heating in a vacuum to 140°. Without further purification, the product gave:

$Cl = 12{\cdot}71$.

$C_{10}H_{19}O_5Cl$ requires $Cl = 13{\cdot}95$ per cent.

The specific rotation in methyl alcohol, which can only, of course, be regarded as approximate, was $[\alpha]_D^{20}$ $+154°$.

On shaking the solution at 20° with silver carbonate, the rotatory power gradually diminished, and in forty-eight hours attained the constant value $[\alpha]_D^{20}$ +40°. The product of the action was a neutral syrup, which was easily recognisable as a mixture of α- and β-tetramethyl methylglucosides, as on hydrolysis with hydrogen chloride the specific rotation increased from +40° to +94° and then diminished to +85°. The sole product of the hydrolysis was tetramethyl glucose.

It was afterwards found that tetramethyl α-methylglucoside might be substituted for tetramethyl glucose in the above preparation, thereby facilitating the process considerably.

Tetramethyl Bromoglucose.—This compound was prepared by the action of phosphorus pentabromide on the sugar, the details of the process being similar to those described above for the chloro-derivative, except that in all the operations the temperature had to be restricted below 80°, as above this the product was decomposed. The substance resembled the chloro-derivative, but was much more unstable; even when preserved in a vacuum and in the dark, complete decomposition took place in a few days. The specific rotation of a freshly prepared specimen in acetone solution was $[\alpha]_D^{20}$ +45·9°. When heated with water at 100°, the compound was completely decomposed with the formation of tetramethyl glucose and hydrogen bromide. Using this reaction as a means of estimating the bromine, analysis gave:

Br = 26·61.

$C_{10}H_{19}O_5Br$ requires Br = 26·75 per cent.

When shaken in methyl-alcoholic solution with silver carbonate, a mixture of the isomeric tetramethyl methylglucosides was obtained, the β-form being produced in large excess. The same result was more rapidly arrived at by heating the bromo-compound with methyl alcohol and silver oxide.

Application of the Grignard Reaction to Tetramethyl Glucose.

On adding a solution of the sugar in dry ether to a similar solution of magnesium methyl iodide, a fairly vigorous reaction ensued, which was continued on a water-bath for thirty minutes. The product was hydrolysed with dilute sulphuric acid and extracted with ether. The ethereal extract after drying over sodium sulphate gave a crystalline residue on evaporation. This was recrystallised several times from light petroleum, and the specific rotation of each crop determined in methyl-alcoholic solution. As in each case the various products melted at 84—85° and gave the constant specific rotation $[\alpha]_D^{20}$ +84°, it was evident that they consisted of the alkylated sugar, over 80 per cent. of which was recovered unaltered.

The authors desire to acknowledge their indebtedness to the Carnegie Trust for a grant in aid of this investigation, and also to Professor Purdie for much valuable advice.

Chemical Research Laboratory,
United College of St. Salvator and St. Leonard,
University of St. Andrews.

XII.—*Studies of Dynamic Isomerism. Part VI. The Influence of Impurities on the Mutarotation of Nitrocamphor.*

By T. Martin Lowry and Egbert H. Magson.

In the first paper of the present series (Trans., 1903, **83**, 1314), a number of experiments were described on the influence of impurities on "The Mutarotation of Glucose." The main conclusion arrived at was that, although alkalis had a very marked accelerating action, the change which the sugar undergoes in solution could not be retarded by the addition of traces of acid, and was therefore due to a specific action of the solvent (conducting water) on the sugar, rather than to alkaline impurities.

In the present paper, a similar series of experiments is described in reference to nitrocamphor, a substance which has the advantage of exhibiting mutarotation in a much larger number of solvents, including inert hydrocarbons, the occurrence of isomeric change in which was known, at least in certain instances, to be dependent on the presence of impurities (Trans., 1899, **75**, 220).

I. *Temperature.*

All the experiments were carried out at 20°. In the case of solutions which changed rapidly, it was convenient to use the ordinary Schmidt and Haensch jacketed tube for making the polarimetric observations; the water circulation could be started before the solution was prepared, so that when transferred to the tube the liquid soon attained the temperature of the water in the jacket. In the case of solutions which changed more slowly, it was not convenient to maintain the water circulation during the whole period of observation, amounting in some instances to several weeks; such solutions were therefore examined in unjacketed polarimetric tubes, of which several could conveniently be stored in the thermostat; when required for observation, these were transferred to a closely-fitting copper jacket, provided throughout with an efficient water circulation. The thermostatic arrangements were identical with those in the two previous series of experiments (Trans., 1906, **89**, 1033). A detailed description of the thermostat, with a diagram of the apparatus, is given in the Transactions of the Faraday Society (1907, **3**, 119).

II. *Materials.*

In spite of their apparent simplicity, the experiments proved to be of an unusually tedious character, owing to the extraordinary difficulty of attaining, and still more of maintaining, the high degree of purification which was necessary, especially in the case of the more inert solvents. This is perhaps scarcely to be wondered at in view of the fact that in a solution of nitrocamphor in benzene there is a distinct response when piperidine is added in the proportion of one part in a hundred million. Again and again the highly purified material was found to have become contaminated in such a way as to undergo isomeric change with greatly increased velocity; the accelerations produced by the addition of small quantities of impurity to an inert solvent could therefore only be determined by laboriously repeating the experiments until concordant observations and successful blank experiments showed that the influence of accidental impurities had been for the most part eliminated.

In the case of solvents, such as alcohol and acetic acid, which actively promote the isomeric change, no such difficulty was experienced. The experiments in chloroform led, on the other hand, to results which were altogether irregular and anomalous; these are described and discussed in the following paper.

The nitrocamphor used in the experiments was purified by crystallising from alcohol until colourless, and then from light petroleum. When practicable, the solvents were distilled from phosphoric oxide in order to remove traces of moisture and basic impurities.

III. *Observations.*

A limited number of observations are recorded in the tables and shown graphically by means of curves. No exact significance is to be attached to the values for the initial and final specific rotations; the solutions were prepared as quickly as possible, and no attempt was made to adjust the concentration accurately, or to allow the solution in the graduated flask to attain an exact temperature before finally adjusting the volume of solvent added. The relative values appear to be accurate in most cases within a few tenths of a degree, but the benzene series compares somewhat unfavourably with the others, owing probably to the exceptionally large values of the rotations to be observed, and their exceptional sensitiveness to small changes of temperature.

The solutions used contained, as a rule, 5 grams of nitrocamphor in 100 c.c. of solution. The rotations were observed in 2-dcm. tubes, and were multiplied by ten in order to obtain the specific rotations of the solutions; an error of 0·1° in the tabulated values corresponds therefore with an error of only 0·01° in the actual polarimeter reading.

IV. *Form of the Curves.*

Although the isomeric change which produces the mutarotation of nitrocamphor is known to involve, at least in certain cases, the presence of a third substance or catalyst, the alterations of rotatory power appear to proceed in every instance according to a unimolecular law. The constant

$$(k_1+k_2)/\epsilon = 1/t\{\log(a_0-a_\infty)-\log(a_t-a_\infty)\}$$

has been calculated for each series of observations and is tabulated in a number of cases. The differences between the observed and calculated values of the specific rotation rarely exceed 0·5° in the alcohol, acetic acid, and ether series, but occasionally rise to 1° and over in the benzene series. Even in the latter case, however, the variations are irregular and the larger errors appear to be due to increased experimental difficulties, and not to any steady deviation from the unimolecular law. The main conclusion to be drawn from this result is that, whatever the nature of the agent by which the isomeric change is brought about, the quantity remains constant throughout the experiment.* The fact that the neutral nitrocamphor becomes converted (to the extent of about one-sixth) into an acid isomeride does not therefore affect the rate at which the change takes place; in other words, "autocatalysis" can only play a very insignificant part in the process.

In the following table are shown:

(1). The solvent used in preparing the solution of nitrocamphor.

(2). The logarithmic constant

$$(k_1+k_2)/\epsilon = 1/t\{\log(a_0-a_\infty)-\log(a_t-a_\infty)\},$$

the time being expressed in minutes in every case.

(3). The approximate period occupied by the change of rotatory power. The period taken is that which elapses before 99½ per cent. of the total change has taken place. It is given by the formula $T = \epsilon \log \frac{1}{200}/(k_1 + k_2)$, and represents in most cases a point at which the outstanding change of specific rotation amounts to only 0·1°.

---

* The effects produced by the gradual introduction or elimination of a catalyst are clearly shown in the following paper.

TABLE I.—*Velocity Constants.*

Solvent.	Constant.	Period.	Percentage.
Alcohol (Kahlbaum's redistilled)	0·0048	8 hours	1·31
,, + 1 per cent. H_2O	0·0096	4 ,,	2·61
,, + $N/10^5$ NaOEt	0·0056	7 ,,	1·52
,, + $N/10^4$ NaOEt	0·0101	3½ ,,	2·75
,, + $N/10^2$ NaCl	0·0196	2 ,,	5·33
Acetic acid	0·0025	15 ,,	0·69
,, + 1 per cent. H_2O	0·0080	5 ,,	2·16
,, + 1 ,, Ac_2O	0·0054	7 ,,	1·46
Ether	0·00149	26 ,,	0·405
,, + 1 per cent. H_2O	0·0154	2½ ,,	4·18
Benzene	0·00013	12 days	0·035
,, + $N/10^7$ NC_5H_{11}	0·00027	6 ,,	0·073
,, + $N/10^6$ NC_5H_{11}	0·0030	13 hours	0·72
,, + $N/10^5$ NC_5H_{11}	0·046	1 ,,	12·5
,, + $N/10^4$ NC_5H_{11}	0·23	10 mins.	62·6
,, + $N/10^3$ $C_6H_5{\cdot}NH_2$	0·00019	8 days	0·051
,, + $N/10^2$ $C_6H_5{\cdot}NH_2$	0·00102	39 hours	0·28
,, + $N/10^3$ $CH_3{\cdot}CO_2H$	0·00051	3 days	0·138
,, + $N/10^2$ $CH_3{\cdot}CO_2H$	0·0070	5½ hours	0·19
,, + $N/10$ $CH_3{\cdot}CO_2H$	0·057	40 mins.	15·50
,, + $N/10^4$ $CCl_3{\cdot}CO_2H$	0·00058	2¾ days	0·158
,, + $N/10^3$ $CCl_3{\cdot}CO_2H$	0·0028	14 hours	0·762
,, + $N/10^2$ $CCl_3{\cdot}CO_2H$	0·0113	3½ ,,	3·074
Benzene	0·00018	9 days	0·049
,, + KCl	0·00080	2 ,,	0·22

(4). The percentage of the outstanding change which is accomplished in each minute. This is given by the formula $P = 100(k_1 + k_2)$, and is obtained by multiplying the logarithmic constant by 100ϵ.

V. *Influence of Water.*

The effect on the velocity of isomeric change of small quantities of water was tested in the case of alcohol, ether, and acetic acid. The alcohol used was Kahlbaum's absolute alcohol (99·8 per cent.), redistilled from oxalic acid in order to remove alkaline impurities. The ether, which had already been distilled from sodium, was redistilled from phosphoric oxide. The acetic acid was purified by distilling from potassium permanganate, and dried by crystallising until the freezing point became constant; it was then redistilled and stored in a Jena glass bottle. In each case, it was found that the addition of water produced a marked acceleration of the isomeric change.

The addition of 1 per cent. of water to the alcohol exactly doubled the velocity of isomeric change, the constant $(k_1 + k_2)/\epsilon$ rising from 0·0048 to 0·0096. The acceleration was almost identical with that produced by the addition of $N/10{,}000$ sodium ethoxide, which gave $(k_1+k_2)/\epsilon = 0{\cdot}0101$. It was conceivable that a part of the acceleration might be due to impurities in the water, but as only 1 per cent. of water was added it would be necessary to assume the presence of $N/100$ alkali in the water to account in this way for the acceleration of the isomeric change. On the other hand, it is well known that the velocity of chemical change is greatly influenced by the solvent in which it

TABLE II.—*Alcohol and Acetic Acid.*

Kahlbaum's Abs. Alcohol (99·8 *per cent.*).

Time (min.).	$[\alpha]_D$ Obs.	$[\alpha]_D$ Calc.	Const.
0	—	−28·2°	—
6	−27·3°	27·9	—
21	24·7	25·1	—
40	22·2	22·2	0·00480
60	19·6	19·7	0·00487
90	17·0	16·8	0·00470
120	14·8	14·8	0·00480
152	13·1	13·2	0·00492
181	12·2	12·3	0·00485
213	11·1	11·5	—
250	10·6	10·8	—
280	10·2	10·7	—
306	9·9	10·3	—
∞	9·6	9·6	—
			0·00482

Alcohol + $N/10^5$ NaOEt.

Time (min.).	$[\alpha]_D$ Obs.	$[\alpha]_D$ Calc.	Const.
0	—	−28·1°	—
7	−26·1°	26·3	—
13½	24·7	25·0	—
23⅞	23·2	23·1	0·0054
33½	21·4	21·5	0·0056
47	19·6	19·7	0·0055
65	17·6	17·4	0·0054
98	14·4	14·5	0·0057
119	13·3	13·3	0·0055
151	11·8	11·9	0·0057
182	11·0	11·1	0·0057
253	10·3	10·0	—
362	9·4	9·4	—
∞	9·3	9·3	—
			0·0056

Alcohol + 1 *per cent. Water.*

0	—	−26·6°	—
5	−25·7°	24·8	—
20	20·6	20·5	0·0094
40	16·7	16·6	0·0095
60	13·9	14·1	0·0099
82	12·5	12·3	0·0094
100	11·4	11·4	0·0097
140	10·35	10·3	0·0097
165	9·6	10·0	—
∞	9·6	9·6	—
			0·0096

Alcohol + $N/10^4$ NaOEt.

0	—	−27·8°	—
9½	−24·1°	24·1	0·0103
16	22·0	22·0	0·0101
25½	19·9	19·6	0·0095
38	17·5	17·0	0·0094
52	14·7	14·9	0·0103
90	11·3	11·6	0·0109
155	9·9	9·9	—
230	9·5	9·5	—
∞	9·4	9·4	—
			0·0101

Alcohol + $N/10^2$ NaCl.

0	—	—	—
10	−17·6°	—	—
20	16·8	−16·9°	0·0199
25	15·7	15·0	0·0180
30	13·4	13·4	0·0196
35	11·3	12·1	0·0219
40	11·0	11·1	0·0200
50	10·2	9·7	0·0181
60	9·6	8·8	—
∞	7·2	—	—
			0·0196

Acetic Acid.

0	—	−4·1°	—
10	−3·4°	3·9	—
30	2·7	2·7	0·00251
40	2·2	2·1	0·00240
50	1·4	1·5	0·00263
60	1·0	1·0	0·00251
70	0·3	0·4	0·00265
210	+4·4	+4·3	0·00261
270	5·5	5·4	0·00261
540	7·7	7·5	—
∞	8·0	8·0	—
			0·00254

TABLE II.—*Alcohol and Acetic Acid* (continued).

Acetic Acid + 1 per cent. Water.

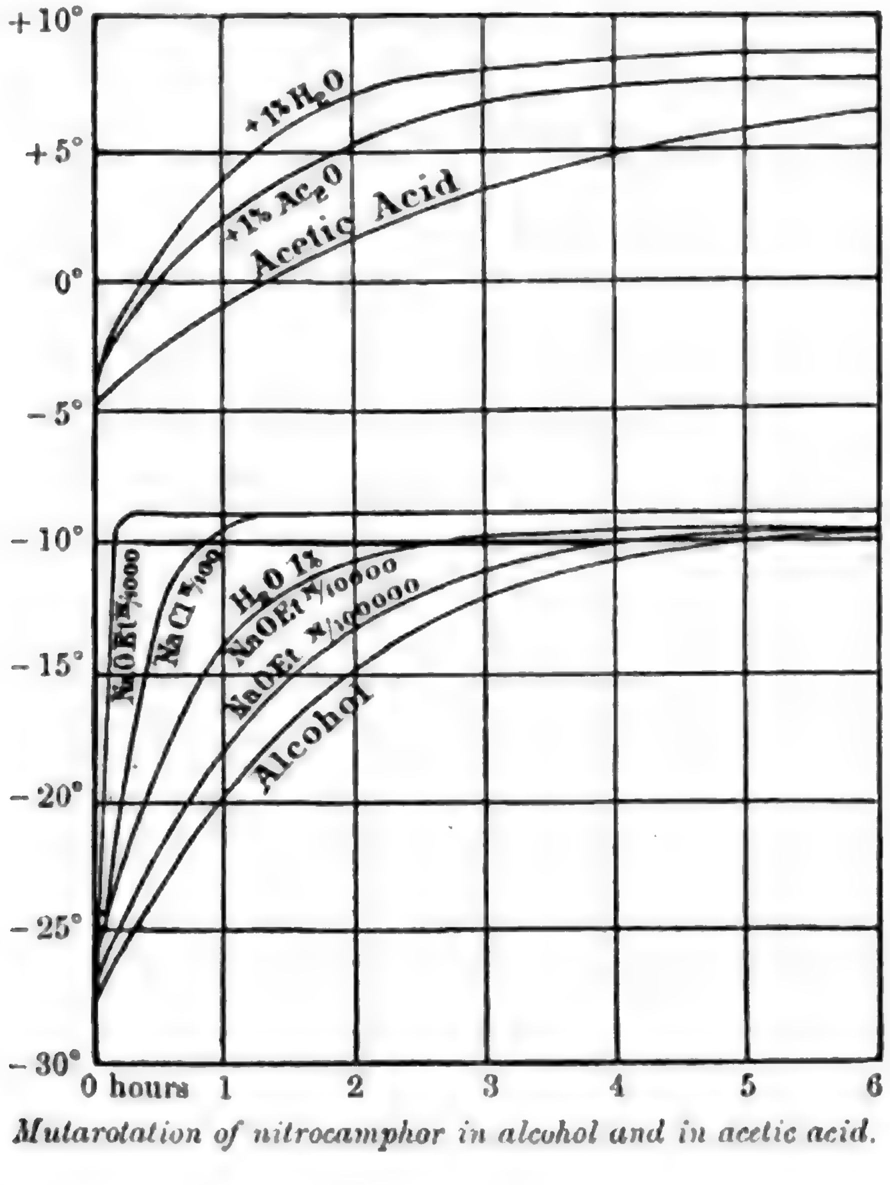
Time (min.).	$[\alpha]_D$. Obs.	$[\alpha]_D$. Calc.	Const.
0	—	—	—
7	−0·9°	—	—
20	−0·4	−0·7°	0·00873
30	+1·1	+0·9	0·00842
40	2·1	2·2	0·00785
50	3·0	3·2	0·00755
60	4·0	4·2	0·00769
70	4·9	5·1	0·00805
80	5·5	5·6	0·00786
90	6·0	6·1	0·00780
100	6·4	6·5	0·00772
180	8·0	8·2	—
300	8·7	8·7	—
∞	8·7	—	—
			0·00796

Acetic Acid + 1 per cent. Acetic Anhydride.

Time (min.).	$[\alpha]_D$. Obs.	$[\alpha]_D$. Calc.	Const.
0	—	−3·6°	—
6	−2·5°	2·8	—
10	1·9	2·2	—
20	1·3	1·1	—
30	0·2	0·0	0·00507
40	+1·0	+0·9	0·00552
50	1·8	1·7	0·00551
60	2·3	2·4	0·00521
80	3·7	3·7	0·00547
100	4·4	4·5	0·00517
120	5·6	5·4	0·00584
180	6·5	6·7	0·00508
300	7·8	7·6	—
∞	7·9	7·9	—
			0·00536

The values for ether and for ether +1 per cent. water are included in table IV of the following paper.

FIG. 1.



Mutarotation of nitrocamphor in alcohol and in acetic acid.

takes place, and the action of water in accelerating the isomeric change on which the mutarotation of nitrocamphor depends (independently of any impurity that might be added with the water) would be in every respect perfectly normal.

In the case of acetic acid, the velocity was increased threefold from 0·00254 to 0·00796 by the addition of 1 per cent. of water. The actual acceleration (0·0054) is, however, very much the same as in the case of alcohol, and the greater ratio is due mainly to a slower velocity of isomeric change in the undiluted solvent.

In the case of ether, the velocity was increased no less than tenfold, from 0·00149 to 0·0154, by the addition of 1 per cent. of water. The greatly increased ratio is, in part, due to the fact that the isomeric change in the undiluted solvent was slower than in the case of acetic acid or alcohol, but the actual increase (0·0139) in the velocity-constant is nearly three times as great as in the preceding cases. The greater activity of the water in this solvent is doubtless to be attributed to the fact that it remains for the most part "free," whereas in alcohol and in acetic acid it is mainly converted into hydrates by combination with the solvent.

VI. *Influence of Alkalis*: *Sodium Ethoxide.*

The isomeric change of nitrocamphor in alcohol proceeds at very much the same rate as the corresponding change which produces the mutarotation of glucose in aqueous solution. As a further coincidence, it is noteworthy that substantially equal accelerations are produced by the addition of sodium ethoxide in the one case and potassium hydroxide in the other. The velocity with which the nitrocamphor changes is increased 16 per cent. by the addition of $N/100,000$ sodium ethoxide to the alcohol, and is almost exactly doubled by $N/10,000$ sodium ethoxide. In presence of $N/1000$ sodium ethoxide, the whole change was complete in about seventeen minutes.

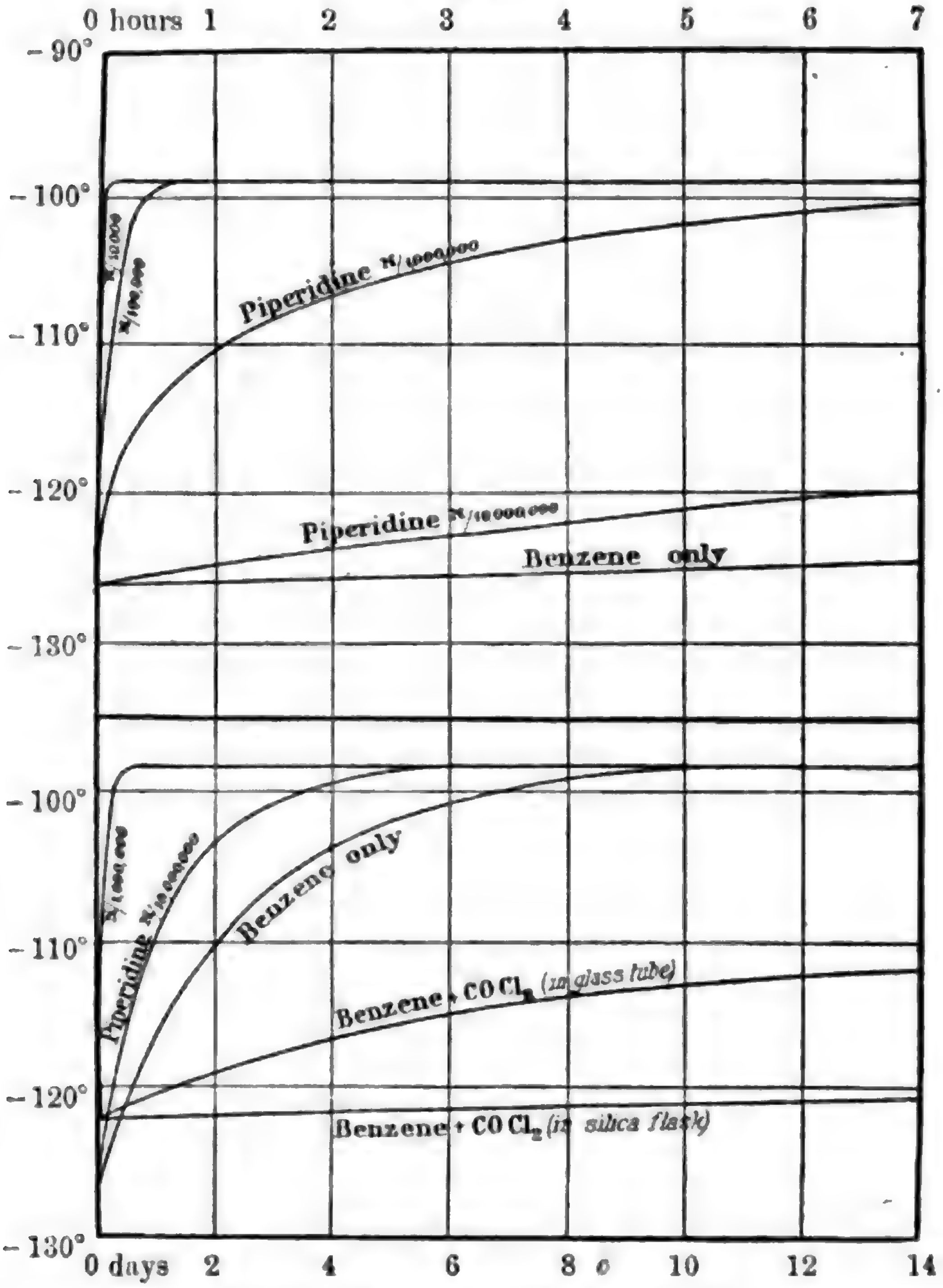
VII. *Influence of Bases*: *Aniline.*

Experiments with aniline, using benzene as solvent, showed that this substance was remarkably inactive in promoting isomeric change. Only the smallest acceleration was produced at a concentration of $N/1000$, and even at $N/100$ the mutarotation was incomplete at the end of twenty-seven hours, although the formation of aniline salt was sufficient to produce a marked alteration in the final specific rotatory power of the nitrocamphor. The actual values of the constants were, for benzene only $(k_1+k_2)/\epsilon = 0·00013$; with $N/1000$ aniline, 0·00019, and with $N/100$ aniline, 0·00102. In spite of the fact that aniline is known to be quite a weak base, it is somewhat extraordinary that the effects which it produces should be one thousand times smaller than those produced by sodium ethoxide in alcoholic solutions.

VIII. *Influence of Bases: Piperidine.*

The experiments with piperidine, using benzene as solvent, proved to be the most remarkable of the series. At a concentration of $N/1000$, which in the case of aniline produced only the slightest acceleration of the isomeric change, piperidine acted so energetically that a steady value for the specific rotation was attained in three minutes, and even with the most rapid working only the first two

FIG. 2.



Mutarotation of nitrocamphor in benzene.

1908.

International Atomic Weights.

		O = 16.			**O = 16.**
Aluminium	Al	27·1	Molybdenum	Mo	96·0
Antimony	Sb	120·2	Neodymium	Nd	143·6
Argon	A	39·9	Neon	Ne	20
Arsenic	As	75·0	Nickel	Ni	58·7
Barium	Ba	137·4	Nitrogen	N	14·01
Bismuth	Bi	208·0	Osmium	Os	191
Boron	B	11·0	Oxygen	O	16·00
Bromine	Br	79·96	Palladium	Pd	106·5
Cadmium	Cd	112·4	Phosphorus	P	31·0
Cæsium	Cs	132·9	Platinum	Pt	194·8
Calcium	Ca	40·1	Potassium	K	39·15
Carbon	C	12·00	Praseodymium	Pr	140·5
Cerium	Ce	140·25	Radium	Rd	225
Chlorine	Cl	35·45	Rhodium	Rh	103·0
Chromium	Cr	52·1	Rubidium	Rb	85·5
Cobalt	Co	59·0	Ruthenium	Ru	101·7
Columbium	Cb	94	Samarium	Sa	150·3
Copper	Cu	63·6	Scandium	Sc	44·1
Dysprosium	Dy	162·5	Selenium	Se	79·2
Erbium	Er	166	Silicon	Si	28·4
Europium	Eu	152	Silver	Ag	107·93
Fluorine	F	19·0	Sodium	Na	23·05
Gadolinium	Gd	156	Strontium	Sr	87·6
Gallium	Ga	70	Sulphur	S	32·06
Germanium	Ge	72·5	Tantalum	Ta	181
Glucinum	Gl	9·1	Tellurium	Te	127·6
Gold	Au	197·2	Terbium	Tb	159·2
Helium	He	4·0	Thallium	Tl	204·1
Hydrogen	H	1·008	Thorium	Th	232·5
Indium	In	115	Thulium	Tm	171
Iodine	I	126·97	Tin	Sn	119·0
Iridium	Ir	193·0	Titanium	Ti	48·1
Iron	Fe	55·9	Tungsten	W	184
Krypton	Kr	81·8	Uranium	U	238·5
Lanthanum	La	138·9	Vanadium	V	51·2
Lead	Pb	206·9	Xenon	Xe	128
Lithium	Li	7·03	Ytterbium	Yb	173·0
Magnesium	Mg	24·36	Yttrium	Yt	89·0
Manganese	Mn	55·0	Zinc	Zn	65·4
Mercury	Hg	200·0	Zirconium	Zr	90·6

th
min

readings of the polarimeter gave higher values. At a concentration of *N*/10,000, isomeric change was complete in about ten minutes, at *N*/100,000 in less than an hour, and at *N*/1,000,000 in about ten hours. Finally, it was found possible by comparing two solutions prepared on the same day and with the same materials to detect a marked acceleration resulting from the addition of piperidine at a concentration of *N*/10,000,000, the velocity constant $(k_1 + k_2)/\epsilon$ being increased from 0·00013 to 0·00026. The constants for the other solutions were, for *N*/1,000,000 piperidine, 0·0030; for *N*/100,000, 0·046, and for *N*/10,000, 0·23. The accelerations produced are roughly proportional to the quantities of piperidine added, but, owing to the exceptional experimental difficulties encountered in this series of observations, we are not able to attach any exact significance to the figures given. The general results are, however, very striking. The proportion of piperidine required to double the velocity of isomeric change is only one part in one hundred million, or 1 decigram per ton. Again, if a comparison be made with the other bases, the piperidine is one hundred times more active than sodium ethoxide dissolved in alcohol, and one hundred thousand times more than aniline dissolved in benzene.

As a further illustration of the activity of the piperidine, it may be noted that in the case of the *N*/100,000 solution the molecules are present in the proportion:

Piperidine : nitrocamphor : benzene = 1 : 25,000 : 1,000,000,

and that about 2 per cent. of the nitrocamphor undergoes change in each minute.* Each molecule of piperidine in the liquid must therefore come into contact with, and invert, 500 molecules of nitrocamphor per minute, and, unless it is selectively guided to the nitrocamphor, it must also collide with at least 20,000 molecules of the solvent.

IX. *Neutral Salts.*

The catalytic action of neutral salts was tested in the case of solutions in alcohol and benzene. In the former case, the alcohol used to dissolve the nitrocamphor was first saturated with salt and filtered; although the quantity of salt dissolved was very small, only 0·08 per cent., corresponding with a concentration of *N*/100, the isomeric change proceeded with four times the usual velocity, the constant being raised from 0·0048 to 0·0196. In the case of benzene, the method adopted was slightly different; 0·1 gram of dry potassium chloride was placed in a flask with 1 gram of nitrocamphor and shaken up with 20 c.c. of benzene; after two or three minutes, the salt was filtered off, and the rotatory power of the nitrocamphor was determined at intervals of ten minutes until a steady value was attained. Here, again, in spite of the minute solubility of the salt, the velocity of change was increased fourfold, the constant rising from 0·00018 to 0·00080.

---

* Equilibrium is reached when about one-sixth of the nitrocamphor has been changed (Trans., 1904, **85**, 1546).

It will be noticed that the salt at a concentration of $N/100$ produced in the alcoholic solution an acceleration three times as great as that caused by sodium ethoxide at a concentration of $N/10,000$. The sodium chloride has therefore an efficiency which is, roughly, 3 per cent. of that of the free alkali.

From these figures, it is possible to deduce an approximate value for the relative affinities of the two acids concerned. The nitro-compound in the 5 per cent. solution had a concentration of $N/4$, whilst that of the chloride was $N/100$; in spite of its twenty-fivefold concentration, the nitrocamphor was able to attach to itself only 3 per cent. of the available base, and is therefore about eight hundred times weaker than the hydrogen chloride.

X. *Influence of Acids.*

The influence of acids was tested in the case of solutions of nitrocamphor in benzene, to which known quantities of acetic acid and of trichloroacetic acid were added. Although the effects produced were smaller than those due to alkalis, it was found that trichloroacetic acid produced a distinct acceleration at a concentration of $N/10,000$ and acetic acid at a concentration of $N/1000$, the velocity-constant being raised from 0·00018 to 0·00058 in the former, and 0·00051 in the latter case.

In the case of the acetic acid solutions, the velocity-constant increased proportionally to 0·0070 and 0·057 when the concentration was increased to $N/100$ and $N/10$. In the case of the trichloroacetic acid, the velocity-constant increased less rapidly than the concentration to 0·0028 at $N/1000$ and 0·0113 at $N/100$. At a concentration of $N/10$ trichloroacetic acid, an anomalous result was obtained. The rotatory power changed much more slowly than in the corresponding acetic acid solution, and actually at a slower rate than at a concentration of $N/100$. An examination of the actual values for the specific rotation revealed the cause of the discrepancy. The trichloroacetic acid solution showed an initial rotation ($[\alpha]_D - 97°$) at fifteen minutes identical with the final rotation of the acetic acid solution; it was therefore probable that the equilibrium between the normal and pseudo-nitrocamphor had already been attained when the first reading was taken, and that the subsequent change of rotatory power was due to the non-reversible change of the "Beckmann" type, whereby the nitrocamphor is converted into the isomeric camphoryloxime (Trans., 1898, **73**, 99). The correctness of this view was proved when in one experiment the rotatory power fell in sixty-three days to ($[\alpha]_D - 26°$), and the oxime actually crystallised out in brilliant needles.

It has previously been recorded (Trans., 1899, **75**, 221) that the addition of a small quantity of hydrochloric acid to a solution of nitrocamphor in commercial alcohol did not cause any marked acceleration of the isomeric change. The difference between the two series of observations is probably due to the fact that in aqueous alcohol the nitro-compound always changes very rapidly, so that the acceleration due to a small amount of acid might easily escape detection, even if the acid itself were not converted into ester; in the benzene solutions, on the other hand, the change is very slow when purified materials are used, and even the mildest accelerating agents are able to produce very marked effects.

TABLE III.—*Benzene.*

(a) *Benzene* only.

Time 0·5 h.	4	22	27	71	93	∞
$[\alpha]_D$ − 126·6°	124·9	119·1	116·2	104·7	102·8	98·2

(b) *Benzene* + $N/10^7$ NC_5H_{11}.

Time 0·5 h.	4	22	27	71	93
$[\alpha]_D$ − 125·0°	121·9	110·7	107·5	100·7	100·2

(c) *Benzene* + $N/10^6$ NC_5H_{11}.

Time 6 m.	13·5	68	188	250	312	430	650	∞
$[\alpha]_D$ − 121·6°	119·1	112·1	106·4	105·2	103·5	102·0	100·5	100·0

(d) *Benzene* + $N/10^5$ NC_5H_{11}.

Time 1·25 m.	2·3	3·5	6·8	23·5	57	∞
$[\alpha]_D$ − 123·0°	121·2	118·5	111·6	103·5	101·4	101·3

(e) *Benzene* + $N/10^4$ NC_5H_{11}.

Time 1·75 m.	2·5	3·5	3·9	4·5	5·0	5·5	6·5	8·2	∞
$[\alpha]_D$ − 107·5°	104·8	102·4	101·5	100·7	99·9	99·1	98·9	98·6	98·4

(f) *Benzene* + $N/10^3$ NC_5H_{11}.

Time 1 m.	1·75	2·6	∞
$[\alpha]_D$ − 100·5°	97·7	96·5	96·5

(g) *Benzene* + $N/10^3$ $C_6H_5NH_2$.

Time 1 h.	7	21	46	59	95	125	141
$[\alpha]_D$ − 125·3°	120·9	111·7	105·2	104·0	102·6	100·3	99·6

TABLE III.—*Benzene* (continued).

(h) *Benzene* + $N/10^2$ $C_6H_5NH_2$.

Time	0·5 h.	2·1	4	6·25	9	22·5	27·75
$[\alpha]_D$	−123·8°	118·1	113·1	107·9	102·7	96·4	96·1

(i) *Benzene* + $N/10^3$ CH_3CO_2H.

Time	22 m.	91	225	575	1240	∞
$[\alpha]_D$	−121·3°	120·5	117·2	108·2	98·9	98·5

(j) *Benzene* + $N/10^2$ CH_3CO_2H.

Time	13 m.	51	90	130	190	315	660	1330	∞
$[\alpha]_D$	−121·5°	118·9	116·4	114·3	113·3	109·8	103·5	100·0	99·6

(k) *Benzene* + $N/10$ CH_3CO_2H.

Time	10 m.	15	20	25	30	40	∞
$[\alpha]_D$	−102·0°	99·0	97·95	97·2	96·9	97·0	97·0

(l) *Benzene* + $N/10^4$ CCl_3CO_2H.

Time	0·3 h.	2·25	4·5	10·5	20·5	∞
$[\alpha]_D$	−123·0°	119·2	117·8	110·2	104·7	98·9

(m) *Benzene* + $N/10^3$ CCl_3CO_2H.

Time	1·1 h.	2·5	4·8	7	13	∞
$[\alpha]_D$	−114·0°	106·9	103·7	100·4	98·9	98·9

(n) *Benzene* + $N/10^2$ CCl_3CO_2H.

Time	0·25 h.	1·75	4·3	∞
$[\alpha]_D$	−114·7°	99·6	96·7	96·7

(o) *Benzene* only.

Time	0·1 h.	4·5	20	42	50	66	114	162	212	∞
$[\alpha]_D$	−123·6°	121·4	113·9	107·7	106·9	105·0	101·8	101·7	101·1	100·0

(p) *Benzene* + KCl.

Time	0·3 h.	1	1·3	2	3	4	6	8	24	46	∞
$[\alpha]_D$	−123·5°	121·4	119·6	118·9	116·8	114·9	112·3	110·0	102·7	100·0	100·0

Summary.

(1) Water has a large effect in accelerating the isomeric change of nitrocamphor dissolved in alcohol, acetic acid, or ether.

(2) The action of alkalis varies considerably, the nitro-compound being excessively sensitive to the most minute quantities of piperidine, but only slightly affected by the addition of considerable quantities of aniline to the benzene solutions; sodium ethoxide in alcoholic solution

produces an intermediate acceleration comparable with that arising from the addition of potassium hydroxide to aqueous solution of glucose.

(3) Neutral salts have a marked accelerating action, possibly on account of the acid properties of the nitro-compound.

(4) Acetic acid and trichloroacetic acid cause an isomeric change, the isomeric change of nitrocamphor dissolved in benzene. In the case of an N/10 solution of trichloroacetic acid, a further large change of rotatory power was caused by the conversion of the nitro-compound into the isomeric camphoryloxime.

XIII.—*Studies of Dynamic Isomerism. Part VII. Note on the Action of Carbonyl Chloride as an Agent for Arresting Isomeric Change.*

By T. MARTIN LOWRY and EGBERT H. MAGSON.

I. *Early Observations of Arrested Isomeric Change.*

IN the paper in which the mutarotation of nitrocamphor was first described (Trans., 1899, **75**, 211), it was stated that solutions in chloroform did not always exhibit this change when first prepared, and that sometimes a considerable period elapsed before the change set in. Thus in one case a 10 per cent. solution in chloroform was kept in a polarimeter tube for a week without the slightest alteration of rotatory power (the actual values of the specific rotation were: twelve minutes, 27·5°; one day, 27·5°; six days, 27·5°; seven days, 27·3°), but at the end of this period the change was started accidentally (apparently by moving the tube), and then proceeded at a moderate rate until at the end of a fortnight the rotation had fallen to 20°, a value midway between the ordinary initial and final values. In a second case, a 5 per cent. solution was prepared in a 25 c.c. graduated flask; half the solution was transferred to a polarimeter tube, and the changes of rotatory power were followed, until at the end of eight days a steady value was attained; after a further period of eight days, when the remainder of the solution was transferred from the flask to a polarimeter tube, the rotatory power was substantially identical with that initially observed sixteen days previously ($[\alpha]_D$ 26·2° as against 27·2°); the transference to the polarimeter tube proved, however, to be sufficient to initiate the change of rotatory power, which proceeded in the normal way towards a steady final value.

From these observations, the conclusion was drawn that, in the case of non-oxygenated solvents, the isomeric change of nitrocamphor did not take place unless some third substance or impurity was present. It was suggested that this impurity might be a base, or, as a less likely alternative, that a trace of the ψ-nitro-compound might suffice to initiate the change of the normal nitrocamphor.

II. *Arrest of Isomeric Change in Acid Chloroform Solutions.*

Nine years later, in the course of the investigation described in the preceding paper, a number of observations were made on the influence of acids and bases on the mutarotation of nitrocamphor dissolved in chloroform. The results obtained were so anomalous and so irregular that it was impossible to draw from them any definite conclusions in reference to the catalytic action of the impurities added. The behaviour of the alkaline chloroform solutions will be referred to later. In the case of the acid solutions, the most striking results were the partial maintenance of the rotatory power during the first few days in a solution containing acetic acid of concentration $N/100$, and the complete arrest of the isomeric change during no less than twenty-four days in a solution to which trichloroacetic acid had been added to a concentration of $N/1000$.

These effects could not be attributed to mere neutralisation of basic impurities, since the ψ-form of the nitro-compound possesses acid properties which would enable it to compete with a mineral acid for possession of an alkali present in quantity insufficient to neutralise both. Again, it has been shown above that neutral salts do actually exert a powerful catalytic action on solutions of nitrocamphor. Finally, it may be noted that the retardations observed in the case of chloroform solutions did not occur when benzene was used as a solvent. The arrest of the isomeric change was therefore due, not to the action of the acid only, but to some action in which the solvent plays an essential part.

It was at first thought that the unique behaviour of the chloroform might be due to a reaction whereby ammonia and aminic impurities were eliminated as hydrogen cyanide or as *iso*nitriles. This action, however, takes place most readily in alkaline solutions, and there was nothing to indicate that the addition of an organic acid would be likely to promote it. The discovery of the actual process by which the isomeric change is arrested was partly accidental. It was noticed that the acid chloroform solutions acquired a powerful and unpleasant odour, and fumed when exposed to the air. Subsequent inquiry elicited the fact that the odour was that of carbonyl chloride, a substance which is produced even in pure chloroform by the action of air and light:

$$CHCl_3 + O = COCl_2 + HCl,$$

and is evidently formed with increased readiness in presence of acids. For some months no importance was attached to this observation, but finally it was realised that carbonyl chloride would be a most efficient agent in eliminating aminic impurities, since these would be converted into neutral carbamides, from which the amine could not be recovered even by the most powerful acids. The presence and the production of carbonyl chloride in the chloroform solutions would therefore afford a sufficient explanation of all the anomalous results which had been obtained (see §§ III and IV), and it was further realised that the chloride might be utilised as a powerful and efficient agent for restraining or arresting isomeric change in other solvents.

III. *Alkaline Chloroform Solutions.*

The observations made with chloroform solutions to which piperidine had been added were at first exceedingly puzzling, but when reconsidered in the light of later knowledge in reference to the action of carbonyl chloride, not only became intelligible, but were found to afford valuable illustrations of the way in which this substance acts in eliminating basic impurities. At moderate dilutions, piperidine is at least as active in chloroform as in benzene, but its activity decreases both with dilution and with time, owing doubtless to its gradual conversion into the carbamide, $CO(NC_5H_{10})_2$. When a freshly prepared *N*/10,000 solution of piperidine in chloroform was used as solvent for the nitrocamphor, a steady value for the specific rotation was obtained within two minutes of the time when the nitro-compound was dissolved; but when the same experiment was repeated twelve days later with the same alkaline solution and the same sample of nitrocamphor, a quarter of an hour elapsed before the final value was reached. The activity of the piperidine in the chloroform had thus been reduced to about one-tenth by merely keeping for a fortnight. For a corresponding solution in benzene, the period occupied by the isomeric change had an intermediate value, about seven minutes. When the dilution of the piperidine was increased to *N*/100,000 by adding a further quantity of chloroform, the change occupied a whole day as compared with an hour for the corresponding solution in benzene. On further dilution to *N*/1,000,000, the rotatory power fell in a single day from 28·0° to 25·4°, but at the end of eight days had only fallen to 22·2°. Further observations at the end of eleven, fifteen, and twenty-one days gave the values 21·9°, 21·8°, and 21·4°, the usual final value being about 15°. In this case, therefore, the rotatory power reached a fictitious final value, and the isomeric change, which had at first proceeded with moderate velocity, was actually arrested, while still far from complete, by the total elimination of the piperidine which had been added in order to promote the change.

TABLE I.—*Chloroform and Piperidine.*

		(a) First sample.		(b) Second sample.					
$N/10^4$	Time	2 m.	∞	3	5	7	12	∞	
	$[\alpha]_D$	−14·9°	14·9	−18·6	17·8	16·3	15·2	13·9	
$N/10^5$	Time	6½ m.	16½	30	46	76	153	210	487
	$[\alpha]_D$	−27·3°	26·7	26·0	25·0	23·4	21·0	20·8	17·3
	Time	710	1500	∞					
	$[\alpha]_D$	−16·1	15·6	14·7					

IV. *Acid Chloroform Solutions.*

At concentrations of $N/10$ and $N/100$, trichloroacetic acid, dissolved in the solvent chloroform, produced accelerations comparable with those observed in the case of benzene solutions, a steady rotation being reached in about half an hour in the former, and a few hours in the latter, case; the velocity constants $(k_1 + k_2)/\epsilon$ were 0·07 and 0·007 respectively. The complete arrest of the isomeric change during twenty-four days at a dilution of $N/1000$, which is clearly shown in the following table, was therefore in marked contrast, not only with the behaviour of the benzene solutions, but also with that of the more acid chloroform solutions.

When acetic acid was added, an acceleration was again shown at a concentration of $N/1000$. At concentrations of $N/10$ and $N/100$, the rotatory power remained almost constant during the first few days, and then changed at a gradually increasing rate towards the ordinary final value. The curve connecting rotatory power with time is therefore horizontal initially as well as finally and contains a point of inflexion, a result that is in accord with the view that the solution was initially free from alkali, but gradually absorbed from the glass a basic catalyst by which the isomeric change was brought about.

TABLE II.—(a) *Chloroform and Trichloroacetic Acid.*

$N/10$	Time	6 m.	14	∞					
	$[\alpha]_D$	−16·8°	14·7	12·5					
$N/10^2$	Time	9 m.	21	61	134	∞			
	$[\alpha]_D$	−17·8°	23·0	18·2	16·5	13·4			
$N/10^3$	Time	15 m.	7 h.	1 d.	2 d.	3	5	6	7
	$[\alpha]_D$	−26·8°	26·9	26·7	26·8	26·7	26·7	26·9	26·7
	Time	8 d.	10	14	16	19	24	64	
	$[\alpha]_D$	−26·8	26·7	26·8	26·4	26·8	26·8	21·8	

(b) *Chloroform and Acetic Acid.*

N/10	Time	5 m.	4 h.	18 h.	24 h.	50 h.	5 d.
	$[\alpha]_D$	−26·7°	26·2	26·1	26·0	25·9	22·0
N/10^2	Time	40 m.	3 h.	16 h.	39 h.	90 h.	
	$[\alpha]_D$	−26·8°	27·1	27·1	26·5	25·7	
N/10^3	Time	1·5 h.	17·5 h.	39·5 h.	87 h.	111 h.	161 h.
	$[\alpha]_D$	−27·5°	25·5	21·2	19·3	17·1	16·5

V. *Arrest of Isomeric Change in Benzene.*

Ever since the first observations were made of the arrest of the rotatory power of nitrocamphor in chloroform, it had been desired to extend the observations to other solvents and other solutes. Hitherto, the only method available had been by the most careful purification of solvent and solute. In the case of solutions prepared by dissolving nitrocamphor in benzene, this purification led to a decrease in the velocity of mutarotation such that a constant rotatory power was only attained after a week or a fortnight, whereas less carefully purified samples attained to equilibrium in the course of a single day. No arrest comparable with those in the chloroform solutions could, however, be observed. Experiments were therefore made to determine whether the desired result could be achieved by adding a trace of carbonyl chloride to the solutions. The chloride, of which a 20 per cent. solution in toluene was purchased, was twice diluted with benzene in the ratio 1 : 200, and the second dilution, in which the carbonyl chloride was present in a concentration of about *N*/10,000, was used as a solvent for a 5 per cent. solution of nitrocamphor. This was prepared in a 50 c.c. flask of silica glass, and a sample was at once transferred to a polarimeter tube. This exhibited a very slow alteration of rotatory power, the change being only half complete at the end of twenty days; the velocity constant $(k_1 + k_2)/\epsilon$ was reduced from values such as 0·00017 or 0·00013 to 0·000024.

After thirteen days, a second sample was transferred from the silica flask to the polarimeter tube; it showed an initial rotation within 1° of that recorded nearly a fortnight previously, but at once commenced to change with a velocity somewhat greater than that of the first sample. At the end of a further eight days, the change had exceeded that undergone by the latter; there was thus accomplished in a week a change which had required three weeks in the case of the first sample.

A third sample, taken from the quartz flask after twenty-five days, showed a further decrease of only 0·4° in twelve days. The velocity constant for the solution in the flask, deduced from the change of

1·4° in twenty-five days, has the extraordinary value of 0·0000008 only.

The analogy to the behaviour of the chloroform solutions is complete; the change normally observed is evidently due to traces of impurity, and, as these can be eliminated by means of carbonyl chloride, they must evidently be aminic in character and not mineral bases. Although the arrest was practically perfect in the silica flask, mineral impurities appeared to be introduced at once on transferring the solution to the polarimeter tube; the velocity of the subsequent change of rotatory power was probably determined by the softness of the glass and the success with which it had been cleaned.

TABLE III.—*Benzene and Carbonyl Chloride.*

(a) *Benzene only.*

Time	¼ h.	6	20⅚	69	98	123	143	169	244	∞
$[\alpha]_D$	−123·1°	120·8	117·8	111·8	108·1	106·8	105·4	104·7	103·45	103·0

(b) *Benzene* + N/10⁴ *Carbonyl Chloride.*

Time	0 h.	14⅓	62	92	117	137	163	279	351	399
$[\alpha]_D$	−122·1°	121·9	117·7	116·5	115·4	115·1	114·9	112·1	111·9	111·7
Time	449 h	502	593	∞						
$[\alpha]_D$	−110·1°	108·4	107·9	103·0						

Second sample.

Time	13 d.	17	19	21
$[\alpha]_D$	−121·1°	114·0	111·1	108·9

Third sample.

25 d.
120·7

Curves representing these observations are included in Fig. 2 of the preceding paper.

VI. *Arrest of Isomeric Change in Ether.*

The velocity of isomeric change in ether had already been reduced by careful purification to less than a tenth of that previously recorded (Trans., 1899, **75**, 222), the period being increased from two hours to a day. The addition of $N/10,000$ carbonyl chloride resulted in a further reduction of velocity in the ratio 1 : 17, the constant $(k_1 + k_2)/\epsilon$ being reduced from 0·00149 to 0·000086. (It is noteworthy that, even in this case, the unimolecular law was found to hold good with a considerable approach to accuracy.) As the solution was prepared in a glass flask and examined in a glass polarimeter tube, there could be little doubt that a large proportion even of the small velocity remaining was due to impurities. This view was confirmed by a subsequent experiment with $N/2500$ carbonyl chloride, which was carried out in a silica flask; in this case, the rotation fell from 40·5° to 28·6° only in fifteen days, and the velocity constant was reduced to 0·000026. It is probable that even this small value might be reduced by further purification, and there can therefore be little doubt that in ether, as in benzene and chloroform, the isomeric change is not spontaneous, but depends on the presence of impurities.

TABLE IV.—*Ether.*

Time mins.	Obs.	Calc.	Constant.
Ether alone.			
0	—	—	—
10	36·4°	—	—
25	36·2	36·3°	—
60	34·6	34·8	0·00161
90	33·4	33·6	0·00148
120	32·4	32·5	0·00154
150	31·5	31·6	0·00151
180	30·6	30·7	0·00152
240	29·5	29·2	0·00140
300	28·4	28·0	0·00137
360	27·5	27·0	—
480	25·9	25·5	—
630	25·0	24·3	—
1380	22·6		0·00149
∞	22·6		
Ether + 1% Water.			
0	—	34·7°	—
10	30·4°	30·5	0·0159
20	27·6	27·6	0·0154
30	25·4	25·5	0·0158
40	24·1	24·1	0·0154
50	23·2°	23·1°	0·0150
60	22·5	22·4	0·0148
80	21·5	21·5	—
120	21·0	20·9	—
∞	20·7	—	0·0154
Ether + N/10⁴ Carbonyl Chloride.			
hours.			
0	—	37·7	—
$\frac{1}{6}$	37·5	37·6	—
$1\frac{1}{6}$	37·4	37·5	—
4	36·6	37·0	—
$18\frac{2}{3}$	35·0	34·9	0·00509
66	30·5	30·2	0·00486
96	27·9	28·2	0·00560
121	27·1	27·2	0·00524
141	26·6	26·5	0·00502
168	25·8	25·8	0·00513
242	24·45	24·6	—
∞	23·9	—	0·00516

In the above table, the logarithmic constant for the carbonyl chloride solution is calculated in hours.

VII. *Arrest of Isomeric Change by Acetyl Chloride.*

In accordance with the explanation put forward above (§ II), the property possessed by carbonyl chloride of arresting isomeric change is due to a specific action on amines and ammonia. Similar properties should therefore be possessed by other acid chlorides which are capable of forming neutral amides. In order to test this, a solution of acetyl chloride in benzene was prepared of *N*/50 concentration, and further diluted to *N*/5000. The second dilution was used as solvent for a 5 per cent. solution of nitrocamphor, which was made up in a silica flask. The first sample transferred to the polarimeter tube showed a change of rotatory power from 126° to 116° in four days, the velocity constant being 0·000025, or about one-sixth of the normal value; the retardation was thus substantially identical with that produced by carbonyl chloride of half the concentration. The solution in the silica flask showed a decrease of rotatory power from 126·0° to 124·1° in five days, corresponding with a velocity constant 0·0000038. At the end of forty-one days, a third sample was taken from the flask; the specific rotation had fallen only 3 degrees in five weeks, the velocity-constant for the whole period being reduced to 0·0000017. The constant for the carbonyl chloride solution under similar conditions was 0·0000008. The acetyl chloride is therefore but little inferior to carbonyl chloride in its "anticatalytic" properties.

It will be noticed that, both here and when carbonyl chloride was used, the arrest of the isomeric change in the solution in the quartz flask was much more marked in the latter than in the earlier stages of the experiment. This is probably due to the fact that the basic impurities on which the isomeric change depends are only very slowly eliminated when their concentration has been reduced, say, to *N*/100,000,000. The gradual elimination of the impurities in these solutions proceeds in a very similar manner to that of the piperidine in the *N*/1,000,000 solution in chloroform described in section III.

Acetyl chloride was also found to be an efficient agent in arresting the isomeric change of nitrocamphor dissolved in carbon disulphide. The disulphide, which had been purified by standing for ten years over concentrated sulphuric acid, was twice distilled from phosphoric oxide and mixed with 1 per cent. of the *N*/50 solution of acetyl chloride in benzene. The *N*/5000 solution obtained in this way was used for preparing a solution of nitrocamphor in a silica flask; the sample transferred to the polarimeter tube changed rapidly, and at the end of four days had attained to a condition of equilibrium; the solution in the flask was found at the end of five days to have undergone no change of rotatory power, the first reading of the second sample being a little higher than the first reading of the rapidly-changing first sample; at the end of forty-one days, the rotatory power had risen, probably by slight evaporation of the solvent, to 89·3°.

TABLE V.—(*a*) *Benzene and Acetyl Chloride.*

		First sample.				Second.	Third.
$N/10^4$	Time	5 m.	8¼ h.	25 h.	100 h.	122 h.	41 d.
	$[\alpha]_D$	−125·9°	125·3	123·8	115·9	−124·1°	−121·0°

(*b*) *Carbon Disulphide and Acetyl Chloride.*

		First sample.					Second.	Third.
$N/10^4$	Time	5 m.	7½ h.	24 h.	46 h.	100 h	120 h.	41 d.
	$[\alpha]_D$	−86·0°	84·8	82·7	82·1	61·3.	−87·0	−89·3°

VIII. *Experiments with Phenylcarbimide.*

The main drawback to the use of acid chlorides as a means of eliminating ammonia and amines is that, in addition to the amide, hydrogen chloride is formed as a product of the interaction, and this, although much less active than the amines, has decided catalytic properties. Another agent which could be used for the purpose, without the formation of any second product, was phenylcarbimide. This was dissolved in benzene and diluted to a concentration of *N*/10,000. When used as a solvent for nitrocamphor, it was found that the rotatory power fell from 124·6° to 114·6° in ten hours, and that at the end of only two days a steady value had been reached. The velocity constant for the solution was 0·00032. The solution in the quartz flask showed a fall of rotatory power from 124·6° to 109·7° in four days, velocity constant 0·000078.

It is evident from these experiments that phenylcarbimide is of no value as an agent for restraining isomeric change. This may be attributed to the fact that it reacts, not only with amines, but also with hydroxylic compounds. The trace of the carbimide added to the benzene would therefore soon condense with ψ-nitrocamphor, and be rendered useless so far as the possibility of eliminating amines is concerned. When present in large quantities, on the other hand, there is little doubt that, whilst reacting with one or both of a pair of dynamic isomerides, it would at the same time eliminate basic impurities and retard or arrest isomeric change (*Brit. Assoc. Report*, 1904, 215). In this way, the definite results obtained by Goldschmidt (*Ber.*, 1890, **23**, 257) when using the agent for the chemical examination of dynamic isomerides may be explained.

TABLE VI.—*Benzene and Phenylcarbimide.*

		First sample.			Second sample.
N/10⁴	Time	0 h.	10¼ h.	∞	3 days
	$[\alpha]_D$	−124·6°	114·6	97·1	−109·8°

IX. *Attempts to Arrest Isomeric Change in Acetic Acid.*

In the case of most of the more active solvents, such as the alcohols, it would be of no use to add an acid chloride as a purifying agent, as it would at once be decomposed by the solvent. In the case of acetic acid, however, it was possible to make experiments, comparable with those carried out in benzene and in ether, by adding to the purified acetic acid either acetic anhydride or acetyl chloride to eliminate ammonia and amines. In the first place, acetic anhydride only was added, the purified acid to be used as solvent for the nitrocamphor being distilled with 1 per cent. of the anhydride. So far from retarding the change, this treatment actually caused an acceleration, owing, perhaps, to the presence of phosphorus compounds in the anhydride. In some later experiments, a trace of acetyl chloride was added to the mixture as it was thought that the anhydride might be somewhat slow in reacting with bases. In this case, also, we failed to produce any definite retardation of the isomeric change. So far as the present experiments are concerned, it appears, therefore, that the methods by which isomeric change may be arrested in benzene, in ether, and in carbon disulphide are not applicable to the group of active solvents to which acetic acid belongs.

TABLE VII.—*Acetic Acid, Acetic Anhydride, and Acetyl Chloride.*

Time	5 m.	10	20	30	40	50	60	70	90	120	180 m.	3½ h.	4½ h.	6½ h.
$[\alpha]_D$	−4·4	3·8	3·2	2·8	2·0	1·15	0·33	+0·2	1·3	2·9	+3·9	4·5	6·9	8·3

NOTE.—The data for acetic acid alone and for acetic acid with 1 per cent. acetic anhydride are included in Table II of the preceding paper.

X. *Theory of Isomeric Change.*

The observations described above, and summarised in Table VIII, have an important bearing on the theory of isomeric change. Up to the present, three chief theories have been advanced.

(1) It was suggested by Laar, in 1885, that in cases such as that under consideration the substance is "tautomeric," that is, in a state of constant oscillation, the mobile hydrogen atom moving constantly to and fro between two alternative positions. Not only therefore was the isomeric change spontaneous, but the isomerides were reduced to "phases," which could not be separated in any conceivable circumstances, unless, possibly, under the inaccessible conditions of the absolute zero.

(2) Eight years previously, Butleroff, in calling attention to the existence of reversible isomeric changes in liquids and solutions, had suggested that these might be (*a*) dependent on the presence of a catalyst, or (*b*) spontaneous.

TABLE VIII.—*Velocity Constants.*

Solvent.	Constant.	Period.	Percentage.
Chloroform + $N/10$ $CCl_3{\cdot}CO_2H$	0·069	33 mins.	18·82
,, + $N/10^2$ $CCl_3{\cdot}CO_2H$	0·0071	5½ hours	1·93
,, + $N/10^3$ $CCl_3{\cdot}CO_2H$	0	∞	0
Benzene	0·00010	16 days	0·0272
,, + $N/10^4$ $COCl_2$ (glass)	0·000024	66 days	0·0065
,, + $N/10^4$ $COCl_2$ (silica)	0·00000078	6 years	0·00021
,, + $N/10^4$ $CH_3{\cdot}COCl$ (glass)	0·000025	64 days	0·0068
,, + $N/10^4$ $CH_3{\cdot}COCl$ (silica)	0·0000017	2 years	0·0005
,, + $N/10^4$ $C_6H_5{\cdot}CNO$ (glass)	0·00032	4¼ days	0·087
,, + $N/10^4$ $C_6H_5{\cdot}CNO$ (silica)	0·000078	20½ days	0·0212
Ether + 1% water	0·0154	2½ hours	4·19
,, only	0·00149	26 hours	0·405
,, + $N/10^4$ $COCl_2$ (glass)	0·000086	18 days	0·0234
,, + $N/2500$ $COCl_2$ (silica)	0·000026	61 days	0·0071

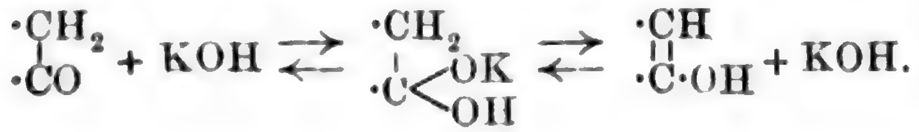
NOTE.—The values marked (glass) are for solutions kept in glass polarimeter tubes. Those marked (silica) are for solutions kept in silica flasks.

(3) The third alternative, suggested in 1899, was an extension to the labile forms of isomerism of the theory of chemical change which Armstrong had applied to the observations of Dixon and Baker in reference to the properties of dried gases. It was suggested that, just as a trace of moisture is necessary, not only for the combustion of phosphorus in oxygen, but even for such simple changes as the combination of hydrogen chloride with ammonia or the reverse dissociation of ammonium chloride, so, also, the transference of a mobile hydrogen atom could only be effected in presence, not merely of a solvent, but also of a catalyst. The experiments now recorded afford the strongest possible confirmation of this view.

Assuming, then, that the isomeric change is caused by a catalyst, two alternative theories are possible in reference to the way in which it acts.

(1) It was conceivable that the essential condition was the "ionisation" or "electrolytic dissociation" of the compound. Thus, if once the hydrogen atom were detached from the molecule, it was possible that the remaining radicle, being endowed with a free valency, might be able to undergo change spontaneously. In this way, the action of alkaline catalysts and the increased velocity of change in ionising solvents could be explained, although the catalytic action of acids would be less easy to understand.

(2) It was possible that the catalyst might combine reversibly with the substance undergoing change, for example, in the case of keto-enolic isomerides with an alkaline catalyst



$$\begin{array}{l}\cdot CH_2\\ \ \ |\\ \cdot CO\end{array} + KOH \rightleftarrows \begin{array}{l}\cdot CH_2\\ \ \ |\\ \cdot C{<}\begin{array}{l}OK\\ OH\end{array}\end{array} \rightleftarrows \begin{array}{l}\cdot CH\\ \ \ \|\\ \cdot C{\cdot}OH\end{array} + KOH.$$

Such an action might take place in presence of any substance capable of being resolved into a hydrogen atom and some other radicle, for example, water, H·OH, alcohol, H·OEt, acetic acid, H·Ac, mineral acids, such as H·Cl, ammonia, $H\cdot NH_2$, or a base, H·OK.

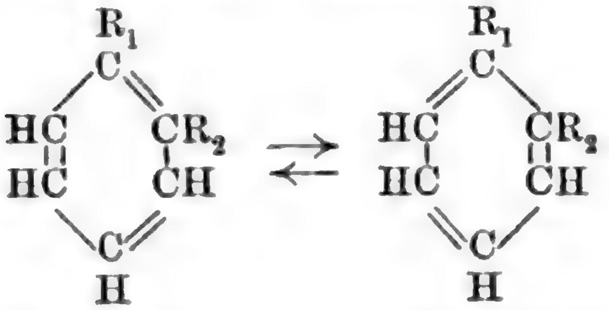
In comparing these two explanations, it should be noted that ether belongs to the class of ionising solvents, since solutions of hydrogen chloride in this liquid possess conducting properties which have been somewhat fully studied. If therefore an ionising solvent were a sufficient cause of isomeric change, it should be impossible, by means of carbonyl chloride or otherwise, to produce any arrest of change in this solvent. In the light of the experiments now recorded, the former explanation appears to be untenable.

On the other hand, the hydrogen compounds enumerated above are just those which exert a powerful catalytic action on the isomeric change of dextrose, nitrocamphor, &c. The catalytic action of acids, of bases, and of water is described in the preceding paper; in the same paper are also shown the rapid isomeric changes which take place in alcohol and in acetic acid as compared with the slow changes in ether, benzene, chloroform, from which a hydrogen atom cannot be separated easily. It is therefore clear that the experimental facts at present established are decidedly in favour of the associative, rather than the dissociative, theory of isomeric change.

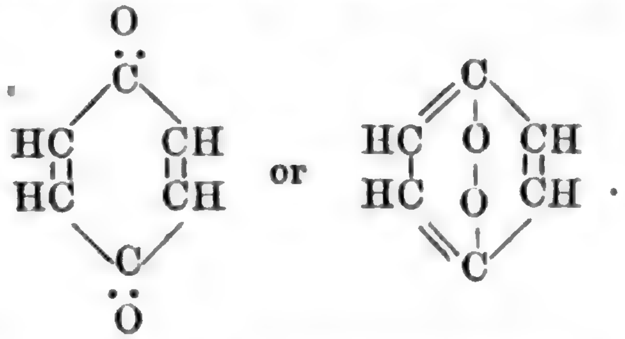
It will be remembered that the presence of water alone does not appear to be sufficient to condition the interaction of hydrogen and oxygen; it is necessary that the water should be sufficiently impure to become an electrolyte. Similar considerations probably apply to the present instance, for example, the effective catalyst is probably, not pure water, but conducting water, not pure acetic acid, but the conducting acid, and so forth. The trace of impurity required to impart conductivity is, however, excessively small, and under most conditions the catalyst will carry with it a sufficient quantity to fulfil this condition, if, indeed, it is not already fulfilled, owing to the presence in the liquid of the two substances involved in the isomeric change.

XI. *Theory of Isomeric Change*: *Isorropesis.*

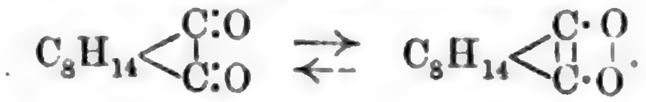
Laar's theory of "tautomerism" has recently been revived by Baly in a special case under the name of "isorropesis." This term has been introduced in order to describe a reversible isomeric change in which the atoms retain their relative positions, but become linked by different valencies. The examples of this type of isomerism most frequently postulated are those of benzene, in which the identity of the 1:2- and 1:6-di-derivatives has been explained by the continuous travelling round the ring of the single and double bonds:



and of quinone, which has been written alternatively:



A simpler example is afforded by camphorquinone:



$$C_8H_{14}<\begin{matrix}C{:}O\\ |\\ C{:}O\end{matrix} \rightleftharpoons C_8H_{14}<\begin{matrix}C\cdot O\\ \| \quad |\\ C\cdot O\end{matrix}.$$

The occurrence of this change has been postulated in order to account for absorption bands in the spectra of certain substances, and, since camphorquinone retains its colour in the solid state, it appears to be implied that isomeric change is still proceeding; the properties assigned to compounds undergoing "isorropesis" are therefore those of "tautomeric" substances in the original sense of the word, and do not correspond in any way with the experimentally established properties of dynamic isomerides.

Whether it will be possible in such cases as these to revivify Laar's discarded theory of tautomerism remains to be seen, but it is at least permissible to question whether even a re-arrangement of bonds can be effected within the molecule and apart from the presence of a catalyst.

Summary.

(1) The active agent in arresting the isomeric change of nitrocamphor dissolved in chloroform is carbonyl chloride, which is produced by oxidation of the solvent in sunlight or in presence of acids. The carbonyl chloride converts ammonia and other aminic impurities into neutral carbamides, and so destroys their catalytic action.

(2) By adding small quantities of carbonyl chloride, it is possible to arrest the isomeric change in other solvents, such as benzene or ether. Acetyl chloride may be used to arrest the change in benzene or in carbon disulphide, but not in acetic acid. Phenylcarbimide produces no retardation in benzene solutions.

(3) The view is advanced that a catalyst is necessary in all cases of

isomeric change. Changes of the keto-enolic type may be effected by water, alcohols, acids, amines, and bases. These substances, which are all of the type HX, probably act by forming additive compounds from which the catalyst may be eliminated in two ways.

(4) Solvents from which a hydrogen atom cannot be eliminated easily are not able to initiate isomeric change, even though, as in the case of ether, they may possess ionising properties.

The expenses incurred during the investigations described in this and in the preceding paper were, in part, defrayed by grants from the Research Fund of the Society and from the British Association; we desire in each case to express our indebtedness for the help thus afforded. We are also indebted to Prof. Armstrong for valuable criticisms, and to Mr. W. P. Paddison for assistance in the experimental work.

WESTMINSTER TRAINING COLLEGE,
LONDON, S.W.

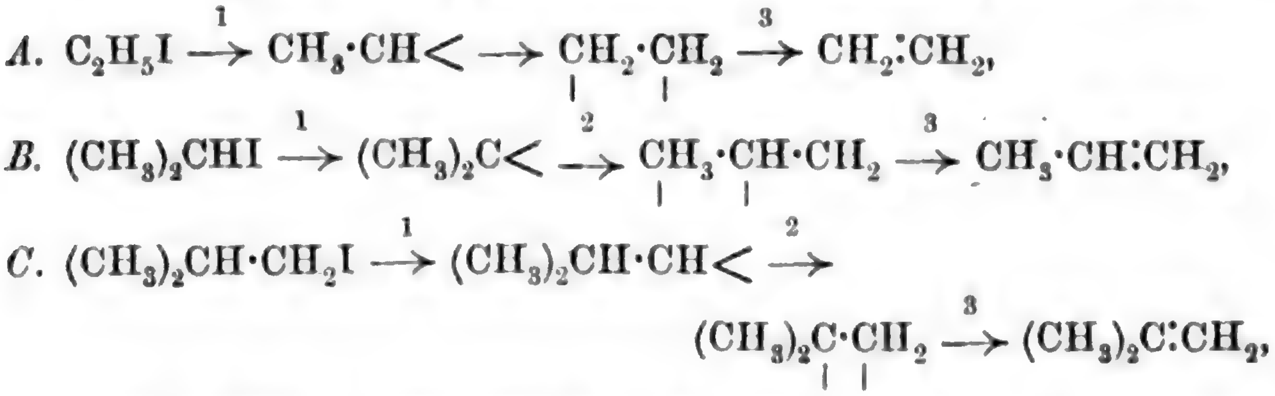
XIV.—*The Effect of Heat on the Alkyl Iodides.*

By ZELDA KAHAN, B.Sc.

SOME years ago, Dr. Travers, wishing to prepare butane, employed for this purpose the well known method of heating together ethyl iodide and zinc. He found, however, that, instead of obtaining pure butane, a mixture of gases was formed, the chief constituent of which was ethane. To investigate the cause of this, a few preliminary experiments were performed, but the work was abandoned owing to lack of time. The investigation of the influence of heat on the alkyl iodides is so much the more important in view of the interesting experiments performed by Nef, and the theory of the bivalent carbon atom based upon them. If it could be proved that in the state of vapour the alkyl iodides are dissociated, it would at least be strong evidence of their being in a similar state in solution. As a result of a large number of experiments (*Annalen*, 1892, **270**, 267; 1897, **297**, 202; 1899, **309**, 126; 1901, **318**, 1), Nef has arrived at the conclusion that all chemical actions, whether of addition or substitution, are to be explained by an application, in each case, of the principle of dissociation. As regards the alkyl halides, Nef assumes that the first stage in their reaction in solution, whatever the other reacting substance may be, is a dissociation into an alkylidene or methylene derivative and the halogen acid; thus a compound of the type $\mathrm{R}{<}^{\mathrm{X}}_{\mathrm{Y}}$ would yield $\mathrm{R}{<} + (\mathrm{X} + \mathrm{Y})$, these two active residues then react with the active residues of the other substance (produced in a similar manner), yielding the observed products of the reaction. Without discussing the large number of interesting experiments performed by Nef in proof of his theory, it may be mentioned that much of the earlier work on the subject is either directly in favour of this theory, or at least of the dissociation of the alkyl halide into olefine and halogen acid. Thus all the facts observed by Frankland in his exhaustive study of the alkyl iodides can be explained very simply on the hypothesis of their dissociation, whereas any other explanation is wholly inadequate to elucidate all the observed facts. Among the most instructive of his experiments are those of the reaction of zinc with ethyl iodide in presence of water, alcohol, and ether. With water, the only gas evolved was ethane, the large number of hydrogen atoms naturally reducing the alkylidene, thus: $\mathrm{MeCH}{<} + \overset{\mathrm{H}-}{\underset{\mathrm{H}-}{|}} = \mathrm{MeCH}_3$, also $\mathrm{MeCH}{<} + \mathrm{H{\cdot}OH} \longrightarrow \mathrm{EtOH}(+\mathrm{MeCH}{<}) \dashrightarrow \mathrm{Et{\cdot}O{\cdot}Et}$, ether, also, being a product of the reaction. As is to be expected, the products of the reaction are the same with alcohol, but with ether, ethylene and butane are also formed. That this explanation is probably the true one is further confirmed by the work of Niederist (*Journ. Chem. Soc.*, 1877, ii, 422); Butleroff (*Compt. rend.*, 1861, **53**, 247); Buckeisen and Wanklyn (*Journ. Chem. Soc.*, 1861, **13**, 140); Erlenmeyer (*Ann. Phys. Chem.*, 1866, **139**, 228); Aronstein (*Ber.*, 1881, **14**, 607; 1880, **13**, 489), and many others.

The most interesting case of all is perhaps the production of ethers and olefines when the alkyl halides react with potassium or sodium ethoxides, or with silver nitrate in alcoholic solution, and in this connexion it might be mentioned that the criticism passed on this theory by Burke and Donnan (Trans., 1904, **85**, 561) on account of Brussof's results (*Zeitsch. physikal. Chem.*, 1900, **34**, 129) is not really valid. Brussof measured the total amount of olefine obtained from the various alkyl iodides under similar conditions, and found that *iso*propyl iodide gave very nearly the same quantity of olefine as *iso*butyl iodide. From this, it would appear that the amount of alkylene dissociation was practically the same for *iso*propyl as for *iso*butyl iodide, whereas, according to Burke and Donnan's experiments, the velocity of reaction for *iso*propyl iodide and silver nitrate in alcoholic solution is at least one hundred and forty times as great as that for *iso*butyl iodide.

Now, although it is true that hydrogen iodide obtained from either kind of dissociation is equally efficient for reacting with silver nitrate, the amount of olefine obtained is not necessarily a measure of the velocity of dissociation; at most, it only shows how readily the butylidene or propylidene passes into the corresponding olefine, thus:



A. $C_2H_5I \xrightarrow{1} CH_3\cdot CH< \longrightarrow \underset{|}{CH_2}\cdot\underset{|}{CH_2} \xrightarrow{3} CH_2{:}CH_2,$

B. $(CH_3)_2CHI \xrightarrow{1} (CH_3)_2C< \xrightarrow{2} CH_3\cdot\underset{|}{CH}\cdot\underset{|}{CH_2} \xrightarrow{3} CH_3\cdot CH{:}CH_2,$

C. $(CH_3)_2CH\cdot CH_2I \xrightarrow{1} (CH_3)_2CH\cdot CH< \xrightarrow{2} (CH_3)_2\underset{|}{C}\cdot\underset{|}{CH_2} \xrightarrow{3} (CH_3)_2C{:}CH_2,$

and what Brussof's experiments show at most is, that in *A* the changes (2) and (3) are less rapid than in *B* and *C*, whilst the two latter may be approximately equal. This result is in complete agreement with Nef's own results (*Annalen*, 1901, **318**, 1). The initial dissociation or its velocity may be far more in one case than another, with consequent production of much acid, but if less olefine is formed, then there is more alkylene available for the production of polymerides or addition products. As a matter of fact, Brussof himself found that the amount of ether formed is the greater the less the olefine evolved. It seems more difficult, however, to account for the fact that, whereas in the reaction of *iso*butyl iodide with alcoholic potash Nef obtained only *iso*butylene but no *iso*butyl ethyl ether, in the reaction with silver nitrate the ether is produced besides butylene. May this fact, however, not depend on the relative stability of the butyl ethyl ether in alkaline and acid solution? The function of the sodium hydroxide, as of the silver nitrate, is, indeed, to remove the hydrogen iodide, but in the case of sodium hydroxide the reacting mixture is throughout an alkaline one, and if the ether is unstable in alkaline solution it would at once break up, thus: $Me_2CH\cdot CH<^{H}_{O\cdot C_2H_5} \longrightarrow Me_2CH\cdot CH< + C_2H_5\cdot OH$; there would thus be a large number of alkylidene residues which would be favourable to the formation of *iso*butylene. Silver nitrate, however, produces the free acid, and this may be favourable to the formation of the ether.

EXPERIMENTAL.

Action of Heat on Ethyl Iodide.

From the foregoing and other work that might be cited, it will be seen that a good deal of the experimental evidence is either in favour of or not against the theory that the first stage in the reaction of the alkyl iodides is their dissociation into halogen acid and alkylidene or alkylene, and the object of the experiments described in this paper was to throw further light on the subject by a more detailed study of the behaviour of the alkyl iodides under the influence of heat. The iodides were generally allowed to stand over silver oxide before redistillation over phosphoric oxide. *iso*Propyl iodide seemed to decompose when distilled over the latter, and had therefore to be dried with calcium chloride; it could, also, never be obtained colourless, unless first decolorised completely with silver oxide. The vapour density of ethyl iodide was first determined by Victor Meyer's method, with the following results, which must be regarded as qualitative only:

Exp.		Temp.	Density.	
I.	Water	100°	78·8	
II.	Aniline	180	79·9 78·6	79·2
III.	Dimethylaniline	192	77·3 76·1	76·7
IV.	Ethyl benzoate	210	72·5 73·9 73·6 74·8 72·1	73·3
V.	Bromonaphthalene	280	62·3 61·2 60·8	Depends on time.
VI.	Diphenylamine Temperature observed	310 305	57·6	

Calculating the percentage dissociation by means of the formula: $a = \frac{100\,(d - D)}{d}$, we find:

Temp.	Extent of dissociation = a.
100°	—
180	—
192	1·1
210	6·4
280	25·1 (density = 62·3)
305	35·4 (density = 57·6)

The increase of dissociation seems to be fairly regular between 192—280°, but at 280°, when there is no longer a sharp end point to the displacement of air, there is evidently some secondary reaction, probably the dissociation of hydrogen iodide or, possibly, of C_2H_5 into $C_2H_4 + H$. Against the latter, it must be said that if C_2H_5 were indeed formed, it should polymerise partly into butane, when the contraction in volume should at least counterbalance the effect of the dissociation. On the other hand, on shaking out the tube with a little water, no acid reaction was obtained. At 280—305°, iodine was formed in the tube, a trace was also found at 210°, whilst below that none was produced.

Ethyl Iodide Heated alone in Sealed Tubes :

A.	Time of heating.	Temp.	Amount removed of KOH.	Ethylene.	Ethane.
I.	5 hours	270°	0·06	0	100
II.	7 ,,	254	0·10	4·6	95·4
III.	3 ,,	270	0·08	0	100
IV.	2½ ,,	254	1·47	25·5	74·0
V.	2½ ,,	210	Amount of gas too small for analysis.		

These results, as well as nearly all those given in this paper, are but typical instances of a large number of similar experiments.

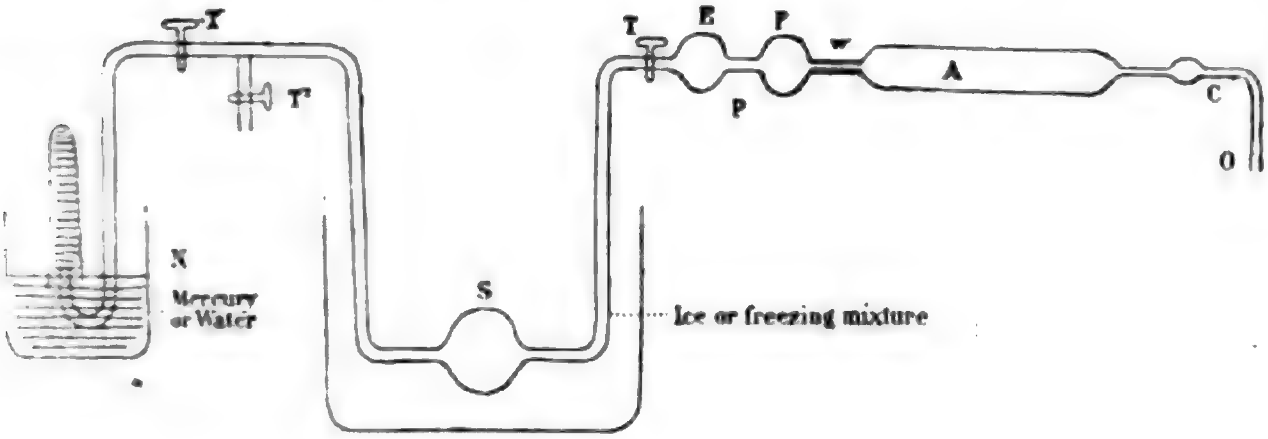
B. A large quantity of gas was next prepared by heating several tubes to 270° for three to five hours, and fractionated by means of liquid air and also liquid air and alcohol, the gas being passed previously through potassium hydroxide; the fractions were then analysed separately. The only product of the reaction was ethane, together with about 0·3 per cent. of hydrogen and about 0·5 per cent. of butane.

C. In these experiments, the tube was heated to about 255° for two hours in the first heating, and to about 270° in each of the subsequent heatings, the excess of gas being removed after each heating :

	1st Heating.	2nd Heating.	3rd Heating.
Ethylene ……	35·7 per cent.	2 per cent.	0 per cent.
Ethane ………	64·3 ,,	90·3 ,,	87 ,,
Butane ………	—	7·0 ,,	trace
Hydrogen ……	—	—	12 ,,
Methane………	—	—	trace
Air ……………	—	trace	trace

D. In this series, an attempt was made to collect the gases while still hot. This was done in order to prevent the prolonged reaction of the constituents while the tube was cooling; it was also hoped to separate, at least partly, the hydrogen iodide, if any were formed, or else the iodine from the hydrogen if it had decomposed, and to prevent the re-association of the first products of the reaction. Moreover, the experiments could be conducted at lower temperatures, and without allowing air to enter the reaction tube at any stage of the reaction. The following apparatus was constructed specially for this purpose.

The tube, *A*, was of the usual kind, and was drawn out to a capillary at *c*, and bent as shown, so that, when the desired quantity of iodide had been introduced through *o*, it could be sealed off at *C*. The capillary tap and tube, *T*, was fused on to *A*, *E* and *F* being only two pieces of ordinary glass tubing joined by a capillary, *P*. The other side of *T* was joined to a capillary tube leading to the arrangement shown, *S* being filled previously with asbestos, and *E* with an easily fusible metal. The air was driven out of *A* through *T* by boiling the ethyl iodide in it. *T* was then shut, and the metal in *E* gently heated and allowed to run into *P*, *F* served to retain any metal that might escape solidification in *P*. This constituted an effective closing of the tube *A*. This device had to be adopted because repeated experiments showed that the taps would not withstand the pressure of the hot vapours and gases produced in *A*. Mercury or water was next introduced through the open end of tube *N* to T^1 by suction at T^2, the latter was then joined to the pump, and the space *T* to T^1 evacuated. When *A* had been heated to the required temperature, the tap, *T*, was opened and *P* heated gently, T^1 being opened simultaneously; the gases from *A* at once forced their way through, and were collected at *N*. As soon as the excess of gas had been evolved, *E* was heated to seal off the tube, which was then re-heated. As grease is dissolved by ethyl iodide, phosphoric oxide was used as a lubricant for the taps, but although the apparatus worked successfully enough, the appearance of the taps showed that they were not air-tight; probably a better result would be obtained by employing taps working in mercury cups, this was not attempted in this series of experiments. As, however,



the air could not have entered the tube, *A*, it may be of interest to give the results of one complete experiment. The thermometer in the furnace indicated 230°, but from the long time taken to reach this point, and from the appearance of the tube, the temperature must have been considerably higher:

	1st Heating, 230° (?).	2nd Heating, 230°.	3rd Heating, 260°.
Ethylene	12 per cent.	6·9 per cent.	0 per cent.
Explosion results after removal of ethylene.			
Gas	7·49 per cent.	4·71 per cent.	2·35 per cent.
Contraction	9·82 ,,	7·71 ,,	5·06 ,,
CO_2	7·41 ,,	5·87 ,,	3·51 ,,
Ratio contraction/CO_2	1·33 ,,	1·31 ,,	1·44 ,,

It was evident that the gas contained air, and this was further confirmed by burning the residual oxygen after the removal of carbon dioxide with phosphorus, when some nitrogen always remained behind, but the results show clearly that more ethylene is obtained at first than on subsequent heatings, and that only small quantities of hydrogen are produced. In the next period, the ethylene has been reduced and less of it is obtained, whilst after the third heating only ethane and hydrogen are produced. The tubes, when heated to 250° for about six hours, or to 270° for a short time, contained a considerable amount of carbon. No carbon was produced in tubes heated to less than 250° or to that temperature for about one to four hours.

Although, from the above experiments, it is to be concluded that hydrogen iodide is one of the products of the reaction, it was scarcely ever directly shown to be present; the water through which the gases were led never giving a decidedly acid reaction. Taking advantage of the fact mentioned by Mendeléeff ("Principles of Chemistry"), that silver chloride is very slowly decomposed by hydrogen iodide at 180°, it was determined to try the action of it on ethyl iodide. If hydrogen iodide is indeed produced, it should act on the silver chloride, forming hydrogen chloride, which, since it does not readily act on ethylene and should not decompose at the temperature, would appear as an end product. This expectation was realised. A tube containing dry silver chloride and ethyl iodide was heated to 250° for three hours. There was considerable pressure on opening the tube, and the water through which some of the gas was passed had a distinctly acid reaction, gave an almost white precipitate with silver nitrate, and with potassium dichromate and sulphuric acid gave the characteristic chromyl chloride reaction. The gas itself before being passed through water fumed slightly in air, and burned with a pale green flame; after removal of hydrogen chloride, the gas consisted of 27 per cent. of ethylene, 70 per cent. of ethane, and 2·6 per cent. of hydrogen. The experiment was repeated several times with exactly similar results.

Action of Zinc on Ethyl Iodide:

Kind of zinc used.	Wt. of Zn in grams.	Wt. of C_2H_5 in grams.	Time and temp.	Ethylene, per cent.	Butane, per cent.	Ethane, per cent.	Hydrogen, per cent.
Stick ……	5	3	100—160° 4½ hours	20	10·4	69·6	0
Stick ……	2	6	100—160° 3½ hours	26·4	3·6	70	0
Powdered…	2	6	100—160° 3½ hours	24·8	20·8	54·4	0
Stick ……	2	6	270° 3½ hours	0	0	96·9	3
Stick ……	6	2	270° 3½ hours	3·2	32·3	64·3	0

It is seen that, although the zinc was always in excess of that theoretically necessary for complete double decomposition into butane and zinc iodide, yet the greater the proportion of zinc employed the greater the amount of butane obtained. It is difficult to explain such a result on the hypothesis of a primary dissociation into R and HI;

two explanations may, however, be given: (1) that, in addition to alkylidene or alkylene dissociation, the iodide is also dissociated to a very slight extent into $C_2H_5 + I$. A large excess of zinc removes the iodine as quickly as formed, leaving a larger number of ethyl groups, which polymerise and form butane. (2) The dissociation is wholly into $R + HI$, but zinc in the active state also exists to a small extent as $>Zn<$, the dotted lines indicating the residual affinity of the zinc atom. The greater the amount of zinc used the larger the number of active atoms of $>Zn<$ present. Then $>Zn< + 2CH_3{\cdot}CH< \rightarrow$ $>Zn<\begin{smallmatrix}CH{\cdot}CH_3\\ CH{\cdot}CH_3\end{smallmatrix} \xrightarrow{HI} \begin{smallmatrix}I\\ I\end{smallmatrix}>Zn<\begin{smallmatrix}CH_2{\cdot}CH_3\\ CH_2{\cdot}CH_3\end{smallmatrix}$, and, zinc iodide being a more stable compound than zinc ethyl, $\begin{smallmatrix}I\\ I\end{smallmatrix}>Zn<\begin{smallmatrix}CH_2{\cdot}CH_3\\ CH_2{\cdot}CH_3\end{smallmatrix} \rightarrow ZnI_2 + C_4H_{10}$. The assumption that zinc can also exist as a quadrivalent element, certainly seems to be rather an improbable one, since the metals of the same and neighbouring groups of the periodic system, if they are ever anything but bivalent, are usually univalent; the suggestion is only made here, because it gives perhaps the most probable explanation of the behaviour of the propyl iodides. On the other hand, there is nothing inherently impossible in the assumption. We know that in the case of many elements, the valencies are not fixed and unalterable. Such a stable bivalent element as oxygen, for example, has been shown to be quadrivalent under certain conditions. Again, the phenomena of double salt formation and of water, alcohol, or ammonia of crystallisation would find an easy explanation by assuming the presence of ordinarily latent residual affinities in the elements. It is thus conceivable that zinc, just like tin, oxygen, or other elements, can act sometimes as though it were quadrivalent (compare also Abegg, *Zeitsch. anorg. Chem.*, 1904, **39**, 330; Marozoff, *J. Russ. Phys. Chem. Soc.*, 1906, **38**, 480). A mixture of the gases obtained as above was also fractionated by means of liquid air, and, in addition to the gases already mentioned, 1—1·5 per cent. of hydrogen and, possibly, 0·5—1 per cent. of methane were also detected.

Action of Sodium on Ethyl Iodide.

One gram of sodium in small pieces was heated with about 3 grams of ethyl iodide at 130—150° for three to four hours. The gas was fractionated and analysed, and the percentage composition was approximately 40 of ethylene, 45 of ethane, 15 of butane, 0·5—1 of hydrogen, and 0·5—1 of methane.

Action of Heat on Methyl Iodide.

Tubes charged with methyl iodide, when heated to 265° for three hours, were found to contain no gas but, when heated to 270° for six hours about 10 c.c. were obtained, which consisted of ethylene and methane, the former varying between 3 and 12 per cent. in the different tubes. Hydrogen iodide was not detected.

Methyl Iodide and Silver Chloride.—The tubes were heated to 275° for five hours; when collected over water, four-fifths of the resulting gas was dissolved, the rest consisting of methane with 2 per cent. of ethylene. A large quantity of gas was prepared, and collected over mercury. Some of it was passed through a little water, which afterwards gave a distinctly acid reaction and an almost white precipitate with silver nitrate. Fourteen per cent. of the gas was absorbed by potassium hydroxide, the rest on fractionation was found to consist of nearly 25 per cent of methane, about 74 per cent. of methyl chloride, mixed with a little methyl iodide vapour, and possibly about 2 per cent. of ethylene and 0·5 per cent. of hydrogen. When the methyl chloride was exploded with oxygen, a thick incrustation of mercuric chloride and a little iodide was formed on the sides of the burette. When the mercury was raised so that it reached this incrustation, a pungent gas with an acid reaction was given off. After this operation had been repeated two or three times, no more gas was evolved. Methyl chloride could have been formed either according to:

(1) $CH_3I + AgCl = AgI + CH_3Cl$ or

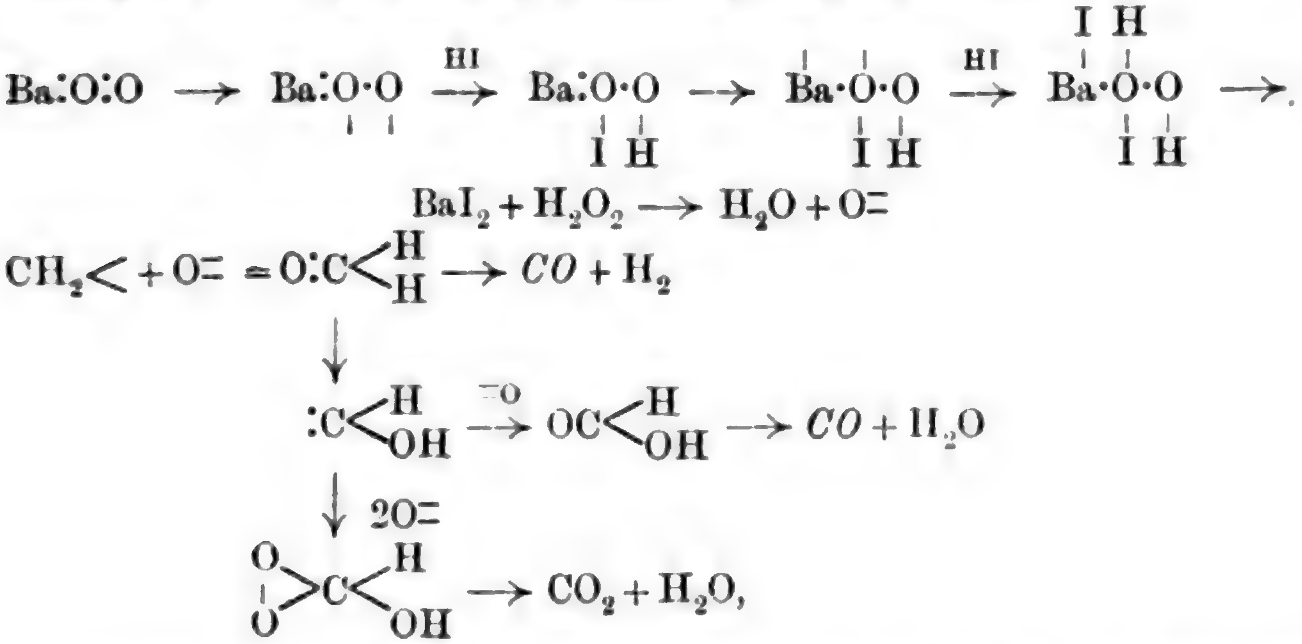
(2) $CH_3I \longrightarrow CH_2\!< + HI$; $HI + AgCl = AgI + \underset{|}{H}\ \underset{|}{Cl}$

$$CH_2\!< + \underset{|}{H}\ \underset{|}{Cl} = CH_2\!<\!\begin{matrix}H\\Cl\end{matrix} \text{ and } CH_2\!< + 2H = CH_4$$

$$\text{and } CH_2\!< + CH_2\!< = C_2H_4.$$

Action (1) is evidently inadequate to explain the production of methane or ethylene; the temperature was too low for a total destruction of methyl iodide, and, even if this were decomposed according to $CH_3I \longrightarrow CH_3 + I$, no methane could be produced unless the reaction $CH_3 \longrightarrow CH_2 + H$ took place, also some ethane should have been formed. If (2) is the actual course of the reaction, then it shows: (1) that methylene combines with hydrogen chloride more easily than ethylene. (2) That methylene unites with other substances more readily than it polymerises, for very little ethylene is produced. (3) That methylene combines with hydrogen chloride as readily as, if not more so than, with hydrogen iodide. In view of the behaviour of ethylene, this seems more unlikely; however, it is quite possible that methylene, as the first member of the series, presents many striking differences from the other members.

Methyl Iodide and Barium Peroxide.—In order to see whether the hydrogen iodide might be oxidised, thus leaving the methylene to remain free or to polymerise, the action of barium peroxide was tried. The result, however, was quite contrary to what had been expected at first. A tube, containing methyl iodide and dry barium peroxide, was heated to about 250°, the resulting gas fractionated with liquid air, and analysed. The percentage composition was 50 of methane, 18 of carbon dioxide, 14 of carbon monoxide, 6·5 of hydrogen, 5·5 of an unsaturated hydrocarbon, probably ethylene, and 6 (by difference) of a higher saturated hydrocarbon, possibly ethane. Although not fulfilling the purpose for which the experiment was started, the results are still interesting, for the question arises as to what gave rise to carbon mono- and di-oxides. Methane is excluded, for it only commences to unite with oxygen at 300°, and then only slowly if kept at that temperature for a week or so (Bone and Wheeler, Trans., 1902, **81**, 535). It is also very unlikely that either ethylene or ethane should be the cause (Trans., 1904, **85**, 693, 1637). If, however, we assume the primary production of methylene and hydrogen iodide, all difficulty disappears, thus we have:



$$\mathrm{Ba{:}O{:}O} \longrightarrow \mathrm{Ba{:}\underset{|}{O}\cdot\underset{|}{O}} \xrightarrow{\mathrm{HI}} \mathrm{Ba{:}\underset{I}{O}\cdot\underset{H}{O}} \longrightarrow \mathrm{\overset{|}{Ba}\cdot\underset{I}{\overset{|}{O}}\cdot\underset{H}{O}} \xrightarrow{\mathrm{HI}} \mathrm{\overset{I}{Ba}\cdot\underset{I}{\overset{H}{O}}\cdot\underset{H}{O}} \longrightarrow$$

$$\mathrm{BaI_2 + H_2O_2 \longrightarrow H_2O + O=}$$

$$\mathrm{CH_2{<} + O= \;=O{:}C{<}^{H}_{H}} \longrightarrow CO + \mathrm{H_2}$$

$$\downarrow$$

$$\mathrm{{:}C{<}^{H}_{OH}} \xrightarrow{=\mathrm{O}} \mathrm{OC{<}^{H}_{OH}} \longrightarrow CO + \mathrm{H_2O}$$

$$\downarrow \mathrm{2O=}$$

$$\mathrm{{}^{O}_{O}{>}C{<}^{H}_{OH}} \longrightarrow \mathrm{CO_2 + H_2O},$$

also $>\mathrm{CH_2} + \mathrm{H_2} = \mathrm{CH_4}$ and $>\mathrm{CH_2} + >\mathrm{CH_2} = \mathrm{C_2H_4} \xrightarrow{\mathrm{H_2}} \mathrm{C_2H_6}$; the last two processes taking place very slowly. This agrees with the property already attributed to methylene of combining with other substances more readily than of polymerising. We should in any case expect methylene to be oxidised and reduced very rapidly.

Methyl Iodide and Zinc.—The results are shown in the following table:

Zinc, in grams.	CH_3I, in grams.	Time and temperature of heating.	Ethylene, per cent.	Ethane, per cent.	Methane, per cent.
2	5	3 hours to 180°	5·5	14·3	80
5·5	3	,, ,,	6·5	38·0	55·5
2	5	,, 275°	1–2	0	98—100

On fractionation of a mixture of these gases, about 0·5 per cent. of hydrogen was also detected. Thus the results are very analogous to those furnished by ethyl iodide, and the reason for obtaining a larger proportion of ethane when a large excess of zinc is used would be the same as that for obtaining butane from ethyl iodide in similar circumstances. On the other hand, the production of methane at such low temperatures can only be explained by assuming the formation of $>CH_2$, and its reduction by the hydrogen iodide. The comparative stability of methyl iodide, and the fact that it is easier to estimate methoxy- than ethoxy-groups by Zeisel's method (Decker, *Ber.*, 1903, **36**, 2895; Perkin, Trans., 1903, **83**, 1367), find an explanation in the readiness with which methylene unites with other elements. This view is further supported by the experiments of Moureu and Valeur on the reaction of sparteine with methyl and ethyl iodides with and without the corresponding alcohols as solvents (*Compt. rend.*, 1905, **141**, 49), and by those of Chablay with methyl chloride and sodamide (*Compt. rend.*, 1905, **140**, 1262).

Experiments with the Propyl Iodides.

Both alone and with metals these decompose much more readily than ethyl iodide. Some of the gas evidently condenses in the reaction tubes, as, when they were opened, a portion of the remaining liquid very soon boiled away. The mercury in the gas holder was attacked almost as soon as the gas entered; on this account, the gases were usually collected over water. When a little mercury was boiled with some of the *iso-* or normal iodide, it was not attacked even after some time. The gas obtained by heating either of the iodides alone fumed in air, a property which it lost after standing over mercury for some time, or directly it was passed through water, the latter in this case giving a distinctly acid reaction. The gas also had a pungent odour, and burned with a pale, peach-coloured, then luminous flame. Evidently hydrogen iodide was contained in it, but the quantity absorbed by water or potassium hydroxide was very small. Most of it was soluble in alcohol.

iso*Propyl Iodide.*—When heated alone for two and a-half hours to 250°, the pressure was so great that, in many cases, the rubber tube connecting the reaction tube to the gas holder burst with a loud report. The gas was fractionated after removal of hydrogen iodide, the uncondensable portion consisted of 1—1·5 per cent. of hydrogen; the rest contained no unsaturated gas, and consisted of pure propane, the explosion results being:

	3·66 gas gave:	C_3H_8 requires:
Contraction,	10·90	10·83
Carbon dioxide,	10·85	10·83
Oxygen used,	18·14	18·05

Tubes heated to 175° from three to six hours gave similar results, the hydrogen being 0·5—1 per cent. In one experiment there seemed to be the possibility of an admixture of a minute quantity of a higher hydrocarbon.

iso*Propyl Iodide with Zinc at* 110°.—The gas did not fume, and was soluble in alcohol, but not in water or potassium hydroxide; it had no acid reaction. It was found to consist of 35 per cent. of propylene, 5 per cent. of hydrogen, and nearly 60 per cent. of propane.

With Sodium.—Schorlemmer (*Proc. Roy. Soc.*, 1867, **15**, 34) remarks that *iso*propyl iodide does not react with sodium even at its boiling point. His experimental conditions were different from those obtaining here, for in a sealed tube at 110° the reaction with sodium was found to be no less marked than with zinc, the gases formed consisting of 53 per cent. of propylene, 2 per cent. of hydrogen, and the rest was pure propane.

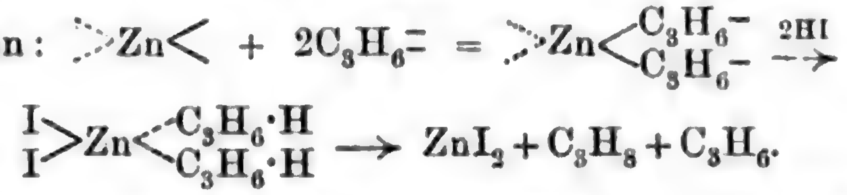
n-*Propyl Iodide Heated alone to* 175°.—The gas formed consisted of pure propane, mixed with 0·3 per cent. of hydrogen and possibly less than 1 per cent. of unsaturated hydrocarbon.

n-*Propyl Iodide with Zinc at* 200°.—The gas consisted of 5 per cent. of hydrogen, 45 per cent. of propane, and 50 per cent. of propylene.

With Sodium.—At 110°, very little gas was formed, although, when the tube containing the sodium and the iodide had been sealed off after boiling out the air, the liquid disappeared in about half an hour, whereas in the case of the *iso*iodide the liquid remained for several days without any change. At 210°, rather more gas was produced, but there was no very great pressure; after removing the excess of gas, the tube was again heated, but no further pressure of gas was observed. The gas obtained at 210° consisted of 46 per cent. of propylene, 48 per cent. of propane, and 5·7 per cent. of hydrogen.

Many attempts were made to isolate the bromide or iodide of diethylethylene, $CH_3{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH_3$, or of tetramethylethylene, $(CH_3)_2C{:}C(CH_3)_2$, from the liquid remaining in the *iso*- and *n*-propyl iodide tubes when heated alone, but with no success. After removing the iodine with potassium hydroxide, a heavy, black oil remained, which was soluble in ether and alcohol. It decomposed on standing, with production of iodine and carbon, and also yielded these products when it was distilled under ordinary or reduced pressure. It probably consists of a mixture of very unstable iodides of complex hydrocarbons, and, perhaps, also of iodides of carbon.

It is remarkable that scarcely any propylene should be formed when the propyl iodides are heated alone, whereas with zinc or sodium nearly half the gas obtained consists of propylene. On the assumption of a dissociation into R + HI, one would expect just the opposite, for the zinc or sodium should decompose the hydrogen iodide as fast as it is formed, leaving as much nascent hydrogen to reduce propylene or propylidene to propane as when the iodides are heated alone. Why, then, should there be more polymerisation in the one case than in the other? If we assume that zinc can exist as $>\mathrm{Zn}<$ in its active state, the reaction becomes easier to understand. For, if the propyl iodides dissociate very easily into propylene and hydrogen iodide, then, when heated alone, there is always sufficient hydrogen iodide to reduce half the propylene or propylidene to propane, leaving the rest free to form complex hydrocarbons or their derivatives; when, however, zinc is present, then:



$$>\mathrm{Zn}< + 2\mathrm{C_3H_6}= \;=\; >\mathrm{Zn}<\begin{matrix}\mathrm{C_3H_6}-\\ \mathrm{C_3H_6}-\end{matrix} \xrightarrow{2\mathrm{HI}}$$

$$\begin{matrix}\mathrm{I}\\ \mathrm{I}\end{matrix}>\mathrm{Zn}<\begin{matrix}\mathrm{C_3H_6\cdot H}\\ \mathrm{C_3H_6\cdot H}\end{matrix} \longrightarrow \mathrm{ZnI_2}+\mathrm{C_3H_8}+\mathrm{C_3H_6}.$$

It might here be remarked that in the case of ethyl iodide, the proportion of ethylene produced is also greater in the presence than in the absence of zinc.

Conclusion.—So far as the behaviour of the alkyl iodides in a state of vapour is concerned, the evidence is wholly in favour of their dissociation into hydrogen iodide and alkylene or alkylidene, which of the two latter is actually formed still being open to doubt. There is, however, nothing to prevent the assumption that they also dissociate to a slight extent into alkyl and iodine as urged by Lobry de Bruyn and Tjimstra (*Zeitsch. physikal. Chem.*, 1904, **40**, 436). In support of the view that the alkyl iodides dissociate, might also be cited the many cases in which their addition or substitution derivatives are formed only, or more readily, in the presence of a strong dissociating agent (compare Mouneyrat, *Compt. rend.*, 1898, **127**, 273; also *Bull. Soc. chim.*, 1899, [iii], **21**, 615; Kronstein, *Ber.*, 1891, **24**, 4245). Most of their reactions in solution are also either in agreement with, or not opposed to, this theory; the only really serious objection being, that the velocity of the reactions in which the alkyl halides take part have mostly pointed to these being bimolecular (Chiminello, *Gazzetta*, 1895, **25**, ii, 410; Bruyn and Steger, *Rec. trav. chim.*, 1899, **18**, 311; Burke and Donnan, *loc. cit.*; Slator, Trans., 1904, **85**, 1286), whereas, since the reaction of, for example, silver nitrate and hydrogen iodide is an ionic reaction, the reaction actually measured should be RI ⟶ R + HI, which would be unimolecular, but, as has been shown by Burke and Donnan, the experimental results do not necessarily justify the assumption that the action is chemically a bimolecular one. Moreover, Slator finds (*loc. cit.*) that the action of ethylene chlorobromide and of ethylene chloroiodide on sodium thiosulphate is unimolecular, and a relatively slow dissociation might explain this at least as well as the assumption he makes of a slow tautomeric change of "α-" $\mathrm{C_2H_4ClBr}$ into "β-" $\mathrm{C_2H_4ClBr}$. On the other hand, the rate and extent of dissociation would naturally depend both on the medium in which the reaction takes place and on the other reacting substance. It is thus quite in accordance with the theory, or at all events not against it, that the velocity of reaction of the alkyl iodides have been found to vary greatly in the experiments of different observers, who have each studied the influence of totally unlike substances on them. If the changes through which the other reacting substance passes during the reaction, take place at measurable and comparative rates, the resulting constant could not be expected to correspond with a unimolecular reaction. The dynamic results do not therefore necessarily disprove the theory, whereas it would be very difficult to explain the results obtained at higher temperatures in any other way. Moreover, by accepting the theory of dissociation in its entirety as applied to all chemical reactions, we have a more rational explanation for such processes as catalysis, many donble decompositions, and substitution.

In conclusion, I wish to thank Prof. Collie for the help he has given me during the progress of this work.

UNIVERSITY COLLEGE, LONDON, W.C.

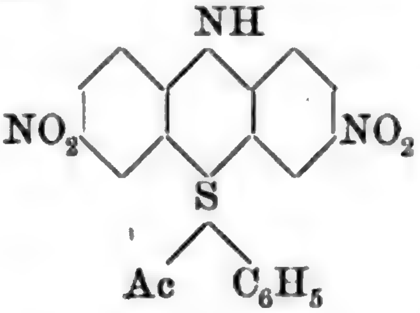
XV.—*Derivatives of* S-*Phenylphenazothionium. Part I.*

By SAMUEL SMILES and THOMAS PERCY HILDITCH.

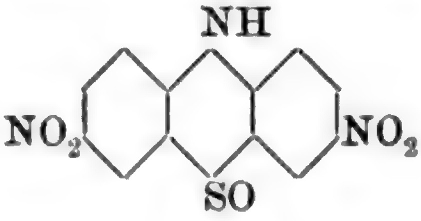
BERNTHSEN (*Annalen*, 1885, **230**, 116) has shown that thiodiphenylamine when treated with concentrated nitric acid is converted to a mixture of two isomeric nitro-compounds of formula: $C_{12}H_7O_5N_3S$. The less soluble of these was called the α-, and the more soluble the β-, derivative. The α-dinitro-compound was shown to contain the nitro-groups in the 3 : 3′-positions by its relationship to the diamino-compound, namely, thionine, which was obtained synthetically in another manner. Bernthsen further showed from a quantitative study of the reduction of the substance that it is probably a sulphoxide, and this view was supported by the consideration that the action of nitric acid on aromatic sulphides in nearly every case furnishes compounds of that nature.

We are now able to advance additional and perhaps more conclusive evidence that these compounds are sulphoxides. It will be shown in the experimental part of the paper, and elsewhere, that either the α- or β-derivatives may be condensed with the simple phenols, phenolic ethers, and aromatic amines, yielding salts of bases, and it has been found (Trans., 1906, **89**, 696; 1907, **91**, 519, 1118) that this reaction is characteristic of the thionyl group.

The products which these dinitrosulphoxides give by condensation with aromatic compounds are of interest, not only on account of their tinctorial properties, but also because they form the first representatives of the *S*-phenylphenazothionium group (I). We have therefore examined these substances more closely; the present paper deals with the product of condensation of the *a*-dinitrosulphoxide (II) with phenetole:

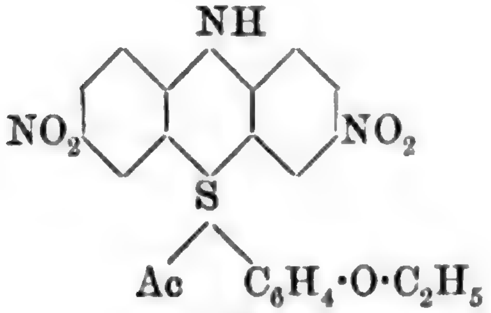


(I.)

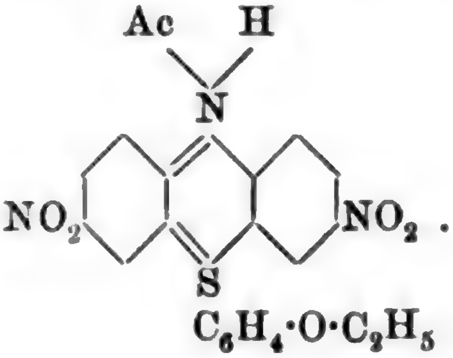


(II.)

If phenetole is added to the solution of this sulphoxide in concentrated sulphuric acid, a green sulphate of a base is formed, and the structure of this product might be represented by either of the following formulæ:



(III.)



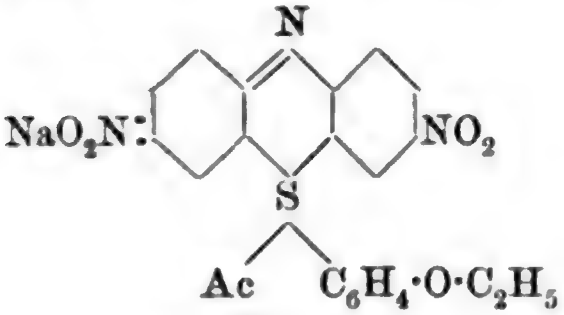
(IV.)

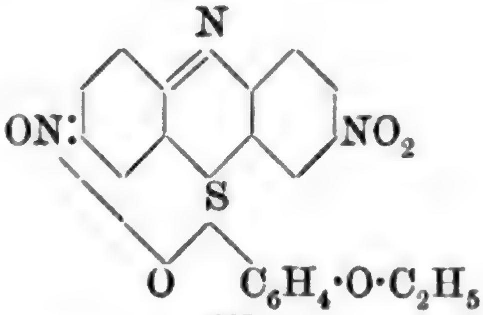
The first of these (III) represents the simple sulphonium salt, which would be directly formed by the change of the thionyl to the sulphonium group; the second (IV) contains the quinonoid sulphonium structure, and this might be formed from the first by rearrangement of the acid group whereby the basic function of the molecule would be transferred to nitrogen. The substance is coloured, and the second alternative contains the quinonoid structure, but, in spite of this, we prefer the first, since all the evidence which can be collected shows that nitrogen in this dinitro-derivative would not be of a basic character. Thus di-*p*-nitrodiphenylamine and di-*p*-nitrodiphenylamine sulphoxide do not exhibit basic properties, but are of acidic nature, forming red salts with alkali hydroxide. Even thiodiphenylamine itself is an extremely weak base, and the hydrochloride, which can only be obtained by the action of dry hydrogen chloride on the ethereal solution, decomposes rapidly on exposure to the air (Unger and Hoffmann, *Ber.*, 1895, **29**, 1365). Further, it may be remarked that the phenetylsulphoxide of di-*p*-nitrodiphenylamine, which is described below, is devoid of basic properties.

When the above-mentioned green salt is treated with aqueous alkali hydroxide, a dark reddish-brown substance of basic character is formed by removal of the elements of the mineral acid from the salt. Now, when di-*p*-nitrodiphenylamine or its sulphoxide is treated with alkali hydroxide, red salts are formed (Störmer and Hoffmann, *Ber.*, 1898, **31**, 2035; Bernthsen, *Annalen*, 1885, **230**, 116, 133), and these undoubtedly have the quinonoid structure,

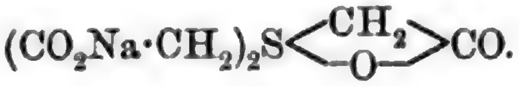
$$NO_2\cdot C_6H_4\cdot N:C_6H_4:NO_2Na,$$

analogous to that of the salts of the nitrophenols. It may therefore be supposed that the green salts in question react with alkali, forming first the quinonoid salt (V):


(V.)

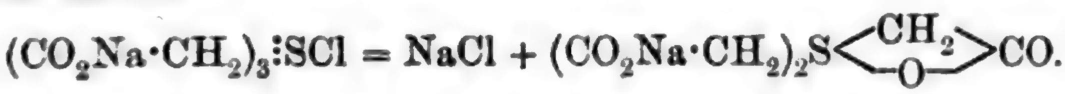

(VI.)

which then, losing the elements of the alkali salt, changes into the nitrothetine (VI). The latter stage in this reaction is analogous to that already observed in the preparation of a carboxythetine. Delisle (*Ber.*, 1892, **25**, 2451) found that the sodium salts of chloroacetic and thiodiglycollic acids interact in warm aqueous solution, giving the sodium salt of dicarboxymethylthetine,



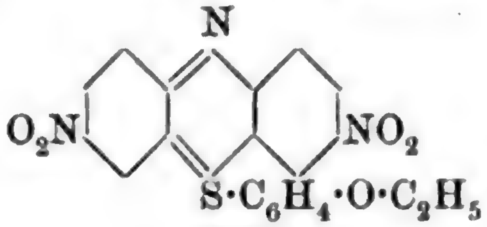
$$(CO_2Na\cdot CH_2)_2S{<}\substack{CH_2\\ O}{>}CO.$$

Here it is evident that the sodium salts first unite to form the trisodium salt of the chloride, which then, losing sodium chloride, passes into the thetine.

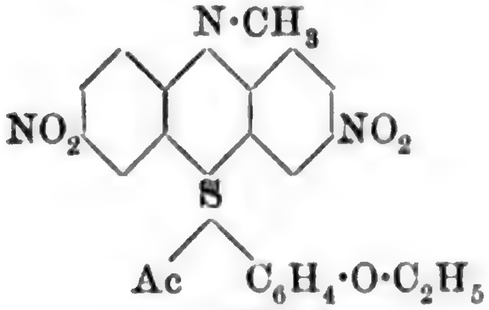


$$(CO_2Na\cdot CH_2)_3\vdots SCl = NaCl + (CO_2Na\cdot CH_2)_2S{<}\substack{CH_2\\ O}{>}CO.$$

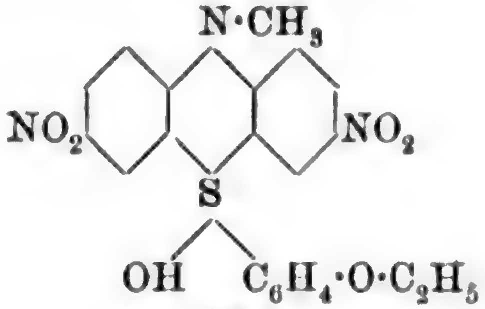
Between the above nitrothetine formula for the base and the alternative sulphonium quinone (VII) there appears to us to be little choice; indeed, it is possible that in solution the


(VII.)

substance is an *iso*dynamic mixture of the two forms. The green salts are also attacked by a large excess of boiling water, undergoing hydrolysis to a bright, crimson base. The product, which is formed from the salt by exchange of the acid group for hydroxyl, contains one molecule of water more than the above anhydride (VI or VII). Solutions of this base are deep red or orange, and exhibit a strong fluorescence. The base obtained by hydrolysis from the sulphate of the *N*-methyl derivative (VIII) must have the constitution (IX):

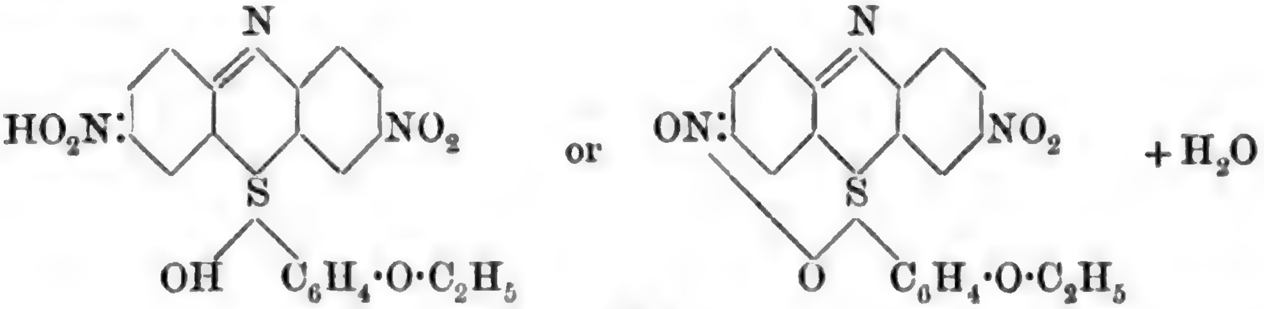


(VIII.)



(IX.)

It has physical properties entirely different from those of the crimson substance mentioned above, being of a dull olive-brown colour and not fluorescent. The base obtained from the unsubstituted salt therefore is almost certainly of different structure, and this may be represented as:



(X.)

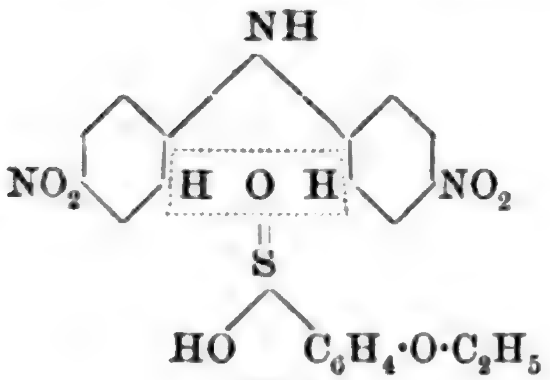
As with other thetines and betaines, it is difficult to determine the nature of this supplementary molecule of water, but it may be remarked that in this case a temperature of 150—180° is required to remove it, and then further decomposition occurs on prolonged heating.

On resuming, it is seen that the green salts (III) are converted by hydrolysis to the red base (X), and by the action of alkali hydroxide to the anhydride (VI), the colour change in either case being accompanied by the formation of the quinonoid structure.

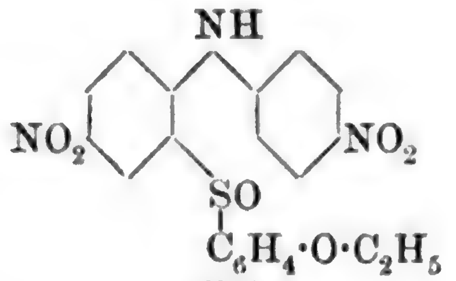
A synthesis of these substances has been attempted in the following manner. It has been previously shown (Smiles and Le Rossignol, Trans., 1906, **89**, 697) that sulphinic acids may be transformed by condensation with certain aromatic substances to aromatic sulphonium bases:

$$R{\cdot}SO{\cdot}OH + 2C_6H_5R' = (C_6H_4R')_2R{\vdots}S{\cdot}OH + H_2O.$$

We therefore hoped that di-*p*-nitrodiphenylamine and phenetole-*p*-sulphinic acid would yield (XI) the salts mentioned above:



(XI.)



(XII.)

Employing the usual condensing reagent, namely, sulphuric acid, it was found that these substances do not interact, but when heated with phosphoryl chloride they yield an olive-green sulphoxide (XII), which forms the intermediate stage in the expected reaction. Efforts to complete the reaction have been unsuccessful, but this is not surprising, for, as will be shown later in other experiments, the formation of sulphonium bases is hindered by ortho-substitution, and, further, there is no doubt that the nitro-groups exert a disturbing influence on the course of the reaction.

The position of the ethoxyl in the *S*-phenyl group of the salts and bases dealt with cannot at present be determined, but, judging from former experience, it almost certainly occupies either the ortho- or para-position with respect to the quadrivalent sulphur atom.

The ease with which the salts of *S*-phenetylphenazothionium are hydrolysed shows the base to be of weak character, and this is in striking contrast to the aromatic sulphonium bases which were formerly examined (Smiles and Le Rossignol, *loc. cit.*). From Kehrmann's experiments on the basicity of derivatives of phenazothionium (*Ber.*, 1906, **39**, 914), it seems certain that the nitro-groups in the above substances would weaken the basicity of the sulphonium group; we hope from the study of other derivatives to ascertain the nature of the parent substance, namely, *S*-phenylphenazothionium.

Since it seems to be a general rule that the introduction of nitro-groups into a fluorescent molecule leads to weakly or non-fluorescent derivatives (Kauffmann, "Die Beziehungen zwischen Fluoreszenz und Chemischer Konstitution," 1906, p. 80), it is worth noticing that the nitro-compounds at present dealt with exhibit this property in a marked degree. In this respect, they are exceptional.

EXPERIMENTAL.

Derivatives of S-*Phenetyl*-3 : 3′-*dinitrophenazothionium.*—The requisite α-dinitrodiphenylamine sulphoxide was obtained by the process recommended by Bernthsen (*loc. cit.*), in which thiodiphenylamine is treated with excess of nitric acid (sp. gr. 1·4). The α-dinitro-sulphoxide is precipitated during the reaction, whilst the β-derivative remains for the greater part dissolved in the mother liquor, from which it may be obtained by precipitation with water. The α-derivative was employed in the following experiments.

S-*Phenetyl*-3 : 3′-*dinitrophenazothionium Sulphate.*—Five grams of di-*p*-nitrodiphenylamine sulphoxide were dissolved in excess of concentrated sulphuric acid; phenetole was then gradually added to the deep yellowish-brown solution, which was kept thoroughly cooled during the reaction. It was found necessary to add a large excess of phenetole, since the greater portion was sulphonated before condensation could take place. The course of the reaction was followed by withdrawing a drop from the mixture after each addition of phenetole and adding it to a few c.c. of cold water; when the condensation was complete, the precipitate was bright bluish-green, and, on the other hand, if much sulphoxide remained condensed the colour was dull brown.

When the reaction was over, the strongly acid solution, now olive-green in colour, was poured into a large bulk of cold water, and the mixture set aside at the atmospheric temperature for a few hours. The bluish-green precipitate of the sulphate was then collected by the aid of the pump, and thoroughly washed with cold water; the yield was almost theoretical. After being dried on a porous tile in a vacuum, the *sulphate* appeared as a bright green powder, which, on further drying at 100°, apparently lost water and was converted into a dark blue substance with metallic lustre. It was slightly soluble in cold water, fairly readily so in alcohol, and, as previously mentioned, was hydrolysed by a large excess of hot water.

Anhydro-S-*phenetyl*-3 : 3′-*dinitrophenazothionium.*—This anhydrous base was obtained from the above sulphate by the action of aqueous alkali hydroxide. The salt was thoroughly triturated with a 5 per cent. aqueous solution of sodium hydroxide at about 25°; the solid base was then filtered from the deep red solution, and washed with cold water until the filtrates were almost colourless and quite neutral towards litmus. After being dried in the steam-oven, the brown solid was purified by precipitation with dry ether from chloroform solution. In this way, the *anhydro-base* was obtained as a brown, crystalline powder with a green metallic lustre; it melted at 221—222°, and was readily soluble in chloroform or alcohol, but very sparingly so in ether or hot water. The fluorescent light emitted by the brown chloroform solution is dull crimson in colour, whilst that of the ethereal solution is bright greenish-yellow; the aqueous solution is purplish-red, but not fluorescent. For analysis, the substance was dried at 100°:

0·1385 gave 0·2976 CO_2 and 0·0515 H_2O. C = 58·60; H = 3·83.
0·1697 „ 0·3631 CO_2 „ 0·0616 H_2O. C = 58·37; H = 4·03.

0·1496 gave 12·7 c.c. of nitrogen at 20° and 761 mm. N = 9·94.
0·2093 ,, 0·1212 $BaSO_4$. S = 7·82.
$C_{20}H_{15}O_5N_3S$ requires C = 58·68 ; H = 3·67 ; N = 10·27 ; S = 7·96 per cent.

S-*Phenetyl*-3 : 3′-*dinitrophenazothionium chloride* was prepared by dissolving the anhydro-base in concentrated hydrochloric acid and precipitating the solution with water. On allowing the salt to separate slowly, it was obtained as a yellowish-green, crystalline powder, which, after repeated precipitation, melted at 202—204°. A dried sample was analysed :

0·1101 gave 0·2168 CO_2 and 0·0372 H_2O. C = 53·64 ; H = 3·76.
0·2065 ,, 0·1028 $BaSO_4$. S = 6·84.
0·1977 ,, 0·0619 AgCl. Cl = 7·74.
$C_{20}H_{16}O_5N_3ClS$ requires C = 53·89 ; H = 3·59 ; S = 7·18 ; Cl = 7·97 per cent.

This *chloride* is soluble in alcohol, giving a blue solution with a crimson fluorescence, which is doubtless due to a small quantity of the anhydro-base, since it vanishes on the addition of hydrochloric acid, the solution then becomes a clear greenish-blue. The action of water on the salt is described later. The compound possesses tinctorial properties ; silk is dyed a pale green tint, which in presence of alkalis becomes reddish-brown.

The *platinichloride* was precipitated as a dark green powder by mixing an alcoholic solution of the chloride with platinic chloride ; it is insoluble in water, but slightly soluble in concentrated hydrochloric acid. After being dried in the steam-oven :

0·1860 gave 0·0290 Pt. Pt = 15·59.
$(C_{20}H_{16}O_5N_3S)_2PtCl_6$ requires Pt = 15·88 per cent.

The *picrate* was obtained by adding an aqueous solution of picric acid to an alcoholic solution of the base. It formed a green powder, which melted at 216—218°, and was insoluble in cold water :

0·1089 gave 0·1982 CO_2 and 0·0299 H_2O. C = 49·63 ; H = 3·05.
$C_{20}H_{15}O_5N_3S,C_6H_3O_7N_3$ requires C = 48·90 ; H = 2·82 per cent.

The *dichromate* was prepared by mixing solutions of the chloride or sulphate with aqueous potassium dichromate. It is an olive-green powder of high melting point :

0·1123 gave 0·0167 Cr_2O_3. Cr = 10·00.
$C_{40}H_{32}O_{17}N_6S_2Cr_2$ requires Cr = 10·04 per cent.

*S-Phenetyl-*3 : 3′-*dinitrophenazothionium Hydroxide*.—When aqueous solutions of the sulphate are boiled, the blue colour changes to red and a crimson precipitate separates. The latter is the thionium hydroxide, which is formed together with mineral acid by hydrolysis of the salt ;

but the reaction, being reversible in presence of acid, is not complete, and a state of equilibrium is attained which can only be disturbed by the addition of alkali or by diluting the solution. To prepare this hydroxide in larger quantity, a concentrated solution of the salt in hot alcohol was poured into a large bulk of water. After the mixture had remained some hours at the ordinary temperature, the crimson precipitate was collected by the aid of the pump, then dried in the steam-oven, and analysed:

A sample prepared from the sulphate gave the following results on analysis:

0·1472 gave 0·3041 CO_2 and 0·0487 H_2O. $C=56·41$; $H=3·71$.

A specimen made from the chloride was also analysed:

0·1245 gave 0·2549 CO_2 and 0·0428 H_2O. $C=55·84$; $H=3·82$.
$C_{20}H_{17}O_6N_3S$ requires $C=56·21$; $H=3·98$ per cent.

The substance is soluble in chloroform or ether with the same fluorescence as that observed in corresponding solutions of the anhydrobase. By spontaneous evaporation, it is deposited from the former solvent in red, feathery needles, which, on heating, darken and contract at 150—180°, and finally melt rather indistinctly at about 220°. When the crystals are powdered, they assume a metallic lustre. The substance does not lose water at 100°, but on heating a sample to 150° for some hours it was found that:

0·3188 lost 0·015 H_2O. $H_2O=4·70$.
$C_{20}H_{15}O_5N_3S,H_2O$ requires $H_2O=4·22$ per cent.

Analysis of the residue showed that some decomposition had taken place at the same time.

S-*Phenetyl*-N-*methyl*-3 : 3′-*dinitrophenazothionium*.—*N*-methylthiodiphenylamine, prepared by methylation of thiodiphenylamine with methyl iodide under pressure (Bernthsen, *Annalen*, 1885, **230**, 88), was converted into the dinitrosulphoxide by the process described by Bernthsen. The latter substance was then treated with phenetole and concentrated sulphuric acid in the manner which has been previously described in the case of the homologous sulphoxide. On pouring the green solution into water, the crude sulphate was precipitated as a sticky, green mass, which rapidly set to a brittle solid. This was separated from the mother liquor, and then triturated with excess of a 5 per cent. aqueous solution of sodium hydroxide. The resulting base was collected by the aid of the pump, washed, dried in the steam-oven, and finally purified by dissolving in chloroform and precipitating the solution with dry ether. S-*Phenetyl*-N-*methyl*-3 : 3′-*dinitrophenazothionium hydroxide* was thus obtained as an olive-brown powder, which melted at about 200°, and was insoluble in ether, but soluble in chloroform or alcohol without fluorescence. The hot dilute aqueous solution is brown:

0·1386 gave 0·2919 CO_2 and 0·0531 H_2O. C = 57·44; H = 4·26.
$C_{21}H_{20}O_6N_3S$ requires C = 57·14; H = 4·31 per cent.

The *chloride* was obtained by mixing the base with excess of hydrochloric acid; it was purified from aqueous alcohol containing a little free hydrochloric acid to prevent dissociation. The substance formed a dark green powder, which was soluble in alcohol, and sparingly so in hot water:

0·1269 gave 0·2530 CO_2 and 0·0492 H_2O. C = 54·80; H = 4·31.
$C_{21}H_{19}O_5N_3ClS$ requires C = 54·84; H = 3·92 per cent.

The *platinichloride* forms a green powder, which is insoluble in water or alcohol:

0·1427 gave 0·0224 Pt. Pt = 15·69.
0·1647 „ 0·2393 CO_2 and 0·0467 H_2O. C = 59·63; H = 3·16.
$(C_{21}H_{19}O_5N_3S)_2PtCl_6$ requires Pt = 15·53; C = 40·13; H = 2·87 per cent.

*Condensation of Di-*p*-nitrodiphenylamine and Phenetyl-*p*-sulphinic Acid.*

The amine was prepared by the process recommended by Goldberg (*Ber.*, 1907, **40**, 4525) for obtaining derivatives of diphenylamine. A mixture of 14 grams of *p*-bromonitrobenzene, 10 grams of *p*-nitroaniline, 5 grams of potassium carbonate, 0·2 gram of copper iodide, and 75 grams of nitrobenzene was heated for twenty hours in a flask provided with a reflux condenser. The dark brown product was distilled in a current of steam to remove nitrobenzene and unchanged bromonitrobenzene; the residue, which solidified on cooling, was collected and repeatedly extracted with concentrated hydrochloric acid. The insoluble, crystalline mass of crude di-*p*-nitrodiphenylamine weighed 10 grams.

Equal weights of phenetole-*p*-sulphinic acid and di-*p*-nitrodiphenylamine were dissolved in excess of phosphoryl chloride, and the brown solution was gradually heated on a sand-bath in a flask provided with a reflux apparatus. The reaction commenced suddenly, the liquid frothing up and becoming bright green; the mixture was boiled for ten minutes longer, and then poured on to pounded ice to decompose the excess of oxychloride. An olive-green solid separated, which was collected, triturated with aqueous alkali hydroxide, thoroughly washed with water, and dried. The substance was purified by precipitation with dry ether from chloroform solution. In this way, *di-*p*-nitrodiphenylamine* 2-p-*phenetylsulphoxide* was obtained as a deep olive-green, crystalline powder, which melted at 170°. It was sparingly soluble in ether and readily so in chloroform or alcohol, giving brown or brownish-green solutions. The colour of the alcoholic solution changed to crimson when aqueous sodium hydroxide was added:

0·1002 gave 0·2067 CO_2 and 0·0384 H_2O. C = 56·27; H = 4·25.
0·1013 „ 0·2092 CO_2 „ 0·0352 H_2O. C = 56·32; H = 3·98.
0·1458 „ 0·0844 $BaSO_4$. S = 7·95.
$C_{20}H_{17}O_6N_3S$ requires C = 56·21; H = 3·98; S = 7·49 per cent.

Derivatives of these substances and other condensation products of the α- and β-sulphoxides are being at present studied, and we hope to publish the results at an early date.

The Organic Chemistry Laboratory,
University College,
London.

XVI.—*The Velocity of Reduction of the Oxides of Lead, Cadmium, and Bismuth by Carbon Monoxide, and the Existence of the Suboxides of these Metals.*

By Francis Joseph Brislee, D.Sc.

The following research was undertaken with the view of determining the conditions under which suboxides are produced by the reduction of higher oxides, by means of carbon monoxide, the velocity of the reduction, and the equilibria existing between the various oxides, carbon monoxide, and carbon dioxide.

Most suboxides, when treated with ordinary chemical reagents, such as acids or alkalis, behave as though they were a mixture of metal and oxide. Lead suboxide, for example, when acted on by an acid, behaves as if it were a mixture of lead and lead oxide. Moist lead suboxide is oxidised to lead hydroxide by the action of air, whereas a mixture of lead and lead oxide remains unchanged under the same conditions. This was first observed by Pelouze and confirmed by later observations.

The conditions for instability and stability of the intermediate suboxides are as follows. If the free energy of the lead suboxide is greater than the sum of the free energy of the lead and the free energy of the lead oxide, then the lead suboxide will tend to decompose into lead and lead oxide. The lead suboxide would, under these conditions, be an unstable compound, and only capable of existence in a metastable state. On the other hand, if the free energy of the lead suboxide is less than the sum of the free energy of the lead and the free energy of the lead oxide, then the suboxide is a stable compound. These conditions may be reversed by a change of temperature, such a "condensed" reaction as the above possessing usually a definite transition-point at a definite temperature.

That the so-called suboxide is not a mixture of lead and lead oxide was proved by Tanatar (*Zeitsch. anorg. Chem.*, 1901, **27**, 304), who determined the heat of solution of the suboxide in acetic acid. He showed that when a mixture of lead and lead oxide is treated with dilute acetic acid, the heat of the reaction is greater than when the suboxide of lead is subjected to the same treatment. From these experiments, Tanatar found that the decomposition of lead suboxide into lead and lead oxide is attended with an absorption of 5·452 Cal. He further showed that the density of the suboxide at 18° is between 8·347 and 8·342, whilst the density of a mixture of lead and lead oxide in the corresponding proportion is 9·973 to 9·979. That the greenish-grey product, obtained by igniting lead oxalate to a higher temperature than that at which the suboxide is formed, is different from the suboxide, although analytically identical, was shown by determining the heat of solution in $N/2$ acetic acid, which was found to be 15·500 Cal., that is, as much as for 1 gram-molecule of lead oxide. Moreover, the density of this product was found to be 9·973 to 9·979, or the same as that of a mixture of lead and lead oxide.

If it be assumed that in a condensed system the total energy change represents very nearly the change of free energy, then it follows that the lead suboxide would be stable with respect to lead and lead oxide.

Preliminary experiments were made on the production of lead suboxide by reducing lead oxide with carbon monoxide at 300°. Carbon monoxide was circulated by means of an apparatus similar to that introduced by Collie (Trans., 1889, **55**, 133), modified by Bone and Wheeler (Trans., 1903, **81**, 535), and used by them for reaction-velocity experiments, over a known weight of pure lead oxide contained in a porcelain boat. The circulation was continued for twenty-four hours, and the temperature was maintained constant at 300°. After cooling, the boat was again weighed; the loss amounted to 3·40 per cent. The product was a velvety, greyish-black powder, which, on treatment with dilute nitric or acetic acid, left a residue of spongy lead. The residue of lead was weighed after digesting the product with dilute acetic acid, and it constituted 48·54 per cent. of the whole. When the substance was moistened with water and exposed to air, it was speedily oxidised to lead hydroxide. The reduction was repeated, using a rather larger quantity of lead oxide, and again the product was identical in its behaviour with that obtained by Tanatar. On still further reduction, the suboxide was gradually reduced to metallic lead. The products of these subsequent reductions were carefully tested for carbonate, but in every case this was found to be absent. This non-formation of carbonate is due to the fact that the partial pressure of the carbon dioxide was always below the dissociation-pressure of lead carbonate. Colson (*Compt. rend.*, 1905, **140**, 865) found that at 280° the dissociation-pressure of lead carbonate is 548 mm., whilst under the conditions of the experiments the partial pressure of the carbon dioxide never exceeded 200 mm.

Further, at the temperature employed, namely, 300°, neither the lead suboxide nor the metallic lead were capable of reacting with the carbon dioxide formed, and experiments made with a view to determining the equilibrium:

$$Pb_2O + CO_2 \rightleftarrows 2PbO + CO \text{ or}$$
$$2Pb + CO_2 \rightleftarrows Pb_2O + CO$$

gave negative results.

Discontinuities in the Rate of Reduction.—Glaser (*Zeitsch. anorg. Chem.*, 1903, **36**, 1) has shown that by the reduction of lead oxide with hydrogen at 211° and 235°, lead suboxide can be obtained, and points out that the reaction:

$$Pb_2O + H_2 = 2Pb + H_2O$$

proceeds much more slowly than the reaction:

$$2PbO + H_2 = Pb_2O + H_2O.$$

The time-reduction curves of lead oxides should show breaks at, or near, the points at which the reduction of one oxide is complete and the reduction of the other commences. For example, if the reduction:

$$2Pb_2O + CO = Pb_2O + CO_2$$

proceeds at a much faster rate than the reduction:

$$Pb_2O + CO = 2Pb + CO_2,$$

then the time-reduction curve should show a break at the point where the lead oxide is completely reduced to lead suboxide. On the other hand, in measuring the rate of reaction in such a system, the rate measured may be the sum of two or more simultaneous reductions; for example, if at first lead oxide is reduced to lead suboxide and a small proportion of the suboxide is also reduced to lead at the same time, but with a different velocity, then the break in the time-reduction curve will occur at the commencement of the second phase of the reaction:

$$Pb_2O \longrightarrow Pb,$$

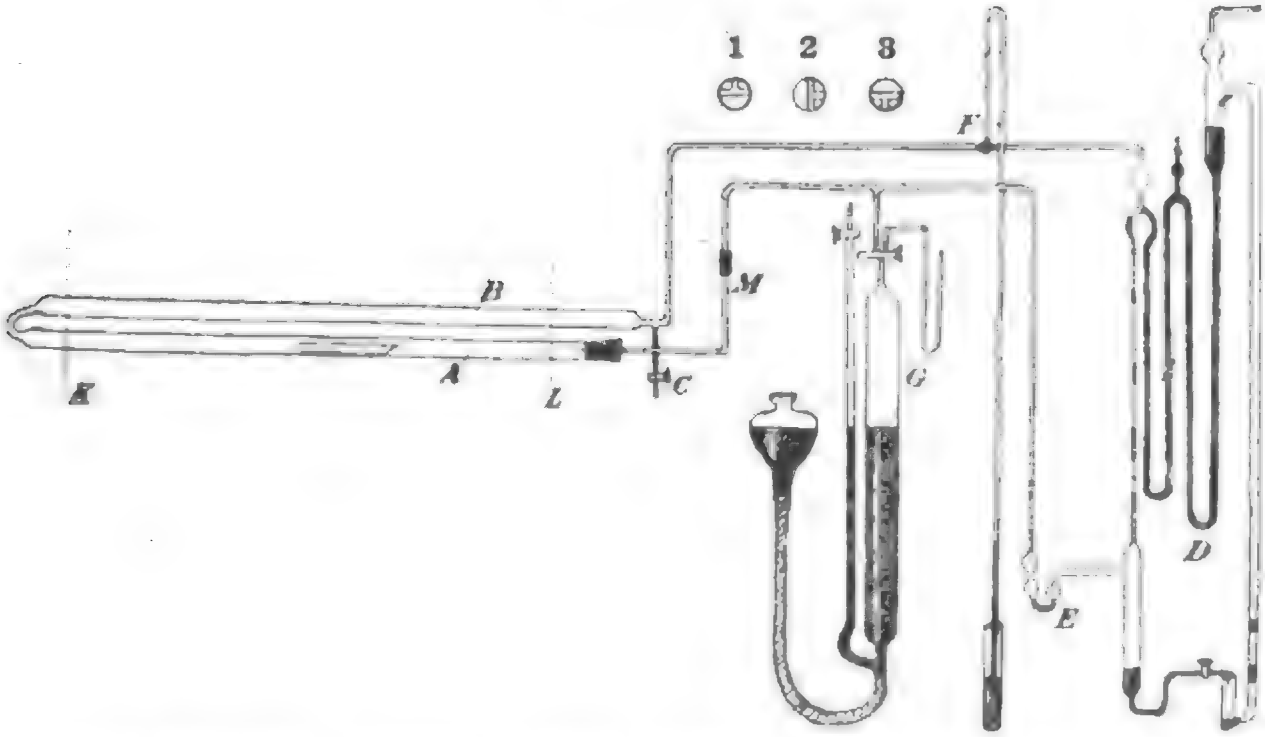
and hence will not exactly coincide with the point at which the higher oxide is completely reduced to the intermediate suboxide.

In the following experiments, the point at which the break in the time-reduction curve occurs is very near the point at which the reduction of the higher oxide ends and that of the lower oxide begins.

EXPERIMENTAL.

The apparatus employed in determining the velocity of reduction is shown in Fig. 1. The tubes *A* and *B* are about 70 cm. long and 2 cm. internal diameter. These tubes were enclosed in a double-jacketed tube furnace, the position of which is denoted by the lines *K* and *L*. The furnace was protected from draughts by sheets of asbestos board, and the gas pressure kept constant by a Stott regulator. Under these conditions, the temperature was maintained at 300°, with a maximum variation of ± 2°. The temperature was measured by a thermometer filled with nitrogen, so placed that its bulb was just between the tubes *A* and *B*, in the neighbourhood of the position of the boat. The thermometer was compared from time to time with an accurate thermoelectric pyrometer. The tubes *A* and *B* were connected with the circulator *D*, which was similar to that introduced by Collie (*loc. cit.*). The tube connecting *B* with the circulator carried a tap, *C*, used for exhausting the apparatus and also for introducing the gas, and a three-way tap connected with a manometer. The tube connecting *A* with the circulator carried a gas sampler, *G*, and the bulbs, *E*, contained a small quantity of mercury by means of which the speed of circulation of the gases could be judged. The whole of the apparatus was joined together by glass connexions, except *A*, which was fitted with a rubber stopper, and there was a joint of stout rubber tube at *M*, wired on, to allow of ready insertion and withdrawal of the boat.

FIG. 1.



The experiments for determining the rate of reduction of the oxides of lead, cadmium, and bismuth were made in the following way. From 2 to 3 grams of the oxide were placed into the porcelain boat in the tube *A*. The rubber stopper was then replaced and the joint *M* wired, and the whole apparatus exhausted as completely as possible by a water-pump connected to *C*. Pure carbon monoxide, prepared from formic acid and concentrated sulphuric acid, was then introduced through *C*, and allowed to escape at the bottom of the manometer and at the tap at the bottom of the circulator. By turning the three-way tap, *F*, into the positions indicated in the diagram by the figures 1, 2, and 3, it was possible to allow the gas to stream through the apparatus in three different directions. In order to ensure complete filling of the apparatus with carbon monoxide, a small quantity of gas was allowed to collect in *G* and was subsequently analysed. When the apparatus was filled with the gas, the tap, *C*, was closed, *F* was turned into the position indicated by (1), and the furnace heated to 300° as rapidly as possible. At this point, the circulator was set in action and the gas circulated for a given time, varying from 1½ to 6 hours, the longer time being used in some of the preliminary experiments, and the shorter when the reduction of the higher to the lower oxide was almost complete. The rate of circulation was kept as constant as possible, and was so regulated that about fifteen bubbles of gas passed through *E* per minute. At the end of the time, the apparatus was allowed to cool, and a portion of the gaseous contents was collected in *G* for analysis, in order to ensure excess of carbon monoxide; in no case was more than one-sixth of the carbon monoxide converted into carbon dioxide. When the apparatus had cooled, the boat was removed and weighed. The purest oxides obtainable were used for the experiments, their purity being checked by analysis.

Reduction of Lead Oxide.

A preliminary experiment was made with the view of determining whether any break occurred in the time-reduction curve at the point at which the composition of the reduction product corresponded to lead suboxide. The reduction was conducted by reducing for six hours at a time, and then weighing the product until the oxide was completely reduced to lead. The quantity of lead oxide used was 2·002 grams, and the gas circulated at the rate of about ten bubbles passing through *E* per minute. The following results were obtained. (These results form a preliminary series only):

TABLE I.

Time in hours ...	0	6	12	18	24	30	36	42	48
Weight in grams	2·002	1·990	1·945	1·916	1·897	1·872	1·870	1·867	1·861

These results are shown in Fig. 2. The break in the curve occurs considerably below the point where the composition of the mixture corresponds to lead suboxide. This may be accounted for by the time elapsing between the several reductions being too long to show the formation of the suboxide as an intermediate phase in the reduction. The above experiment was repeated, the rate of circulation of the gas being increased to about twenty bubbles per minute, and the time of each reduction being reduced to three hours at the commencement and towards the end of reduction. When the reduction of the oxide to suboxide was almost complete, a shorter period of reduction was then used, namely, 1½ hours. The results are given below:

FIG. 2.

Reduction $PbO \rightarrow Pb_2O \rightarrow Pb$.

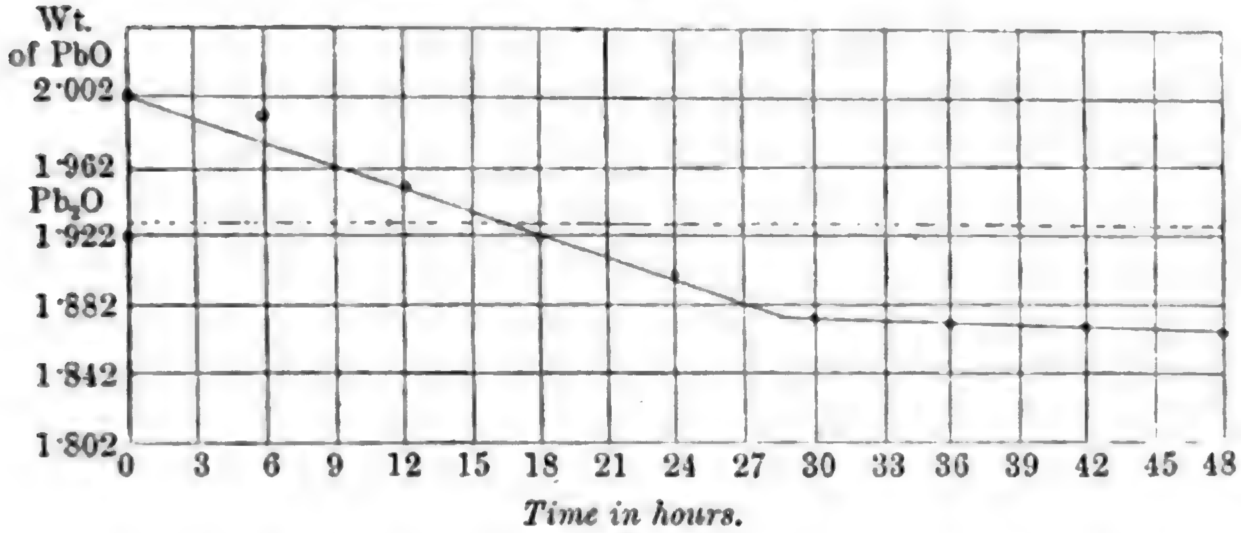


FIG. 3.

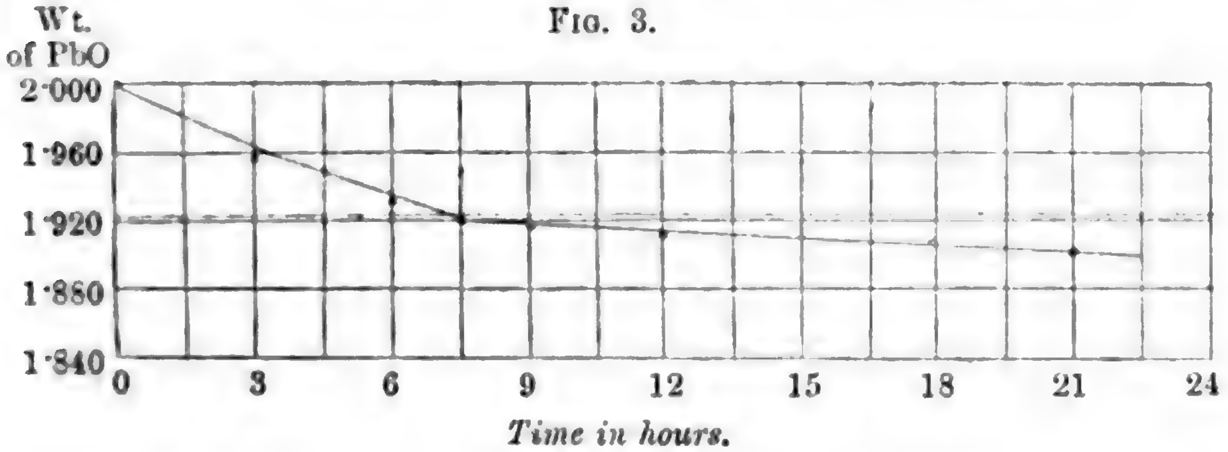


TABLE II.

Time in hours ...	0	3	6	7½	9	12	18	21	30
Weight in grams	2·000	1·957	1·936	1·919	1·917	1·913	1·901	1·896	1·861

Fig. 3 shows these results plotted as a time-reduction curve. The break occurs very close to the point at which the composition corresponds to that of lead suboxide. Additional measurements of the rate of reduction of lead oxide were made, and in every case a break occurred in the neighbourhood of the point corresponding to reduction to lead suboxide. It is probable that surface changes may account for the differences in the form of the curves actually obtained, but the curves all indicate a difference in velocity of the two phases of the reaction, namely:

$$(1)\ PbO \longrightarrow Pb_2O$$
$$(2)\ Pb_2O \longrightarrow Pb.$$

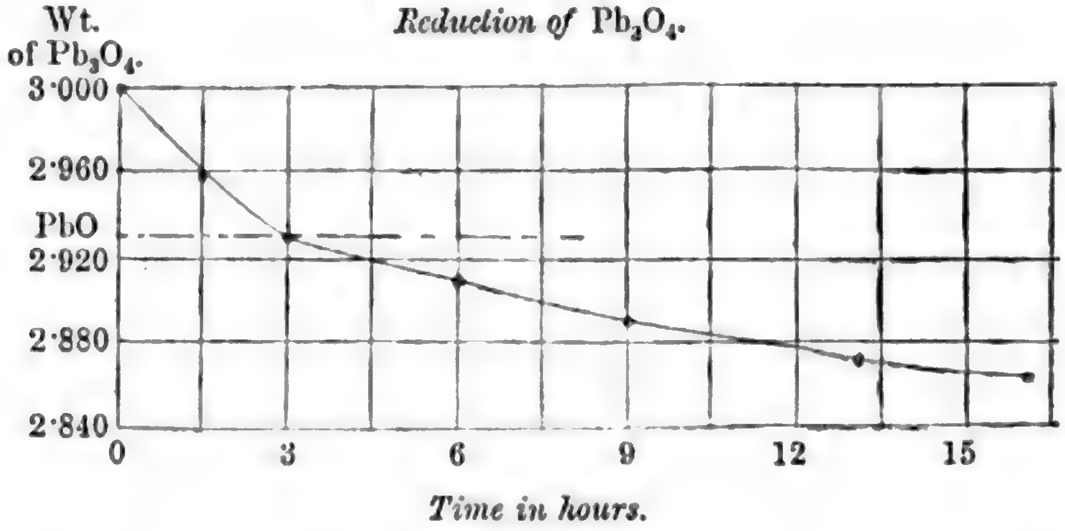
In subsequent experiments, the oxides used were all finely divided, sifted through muslin, and spread in the boat so as to form an even layer 3—4 mm. deep. The rates of reduction were all measured under comparable conditions as regards surface of oxide exposed, temperature, and rate of circulation of the gas.

Reduction of Triplumbic Tetroxide.

The rate of reduction of triplumbic tetroxide was next investigated. The time-reduction curve should show a break at, or near, the point corresponding to complete reduction to lead oxide if the rate of reduction of triplumbic tetroxide to lead oxide is considerably faster than the rate at which lead oxide is reduced to lead suboxide. A preliminary experiment was made, using 3 grams of pure triplumbic tetroxide. The results of this experiment are shown in Fig. 4, the break occurring almost exactly at the point where the composition of the mixture corresponds to lead oxide. When the oxide was removed from the tube for the purpose of weighing, at this point, it had the characteristic yellow colour of litharge.

FIG. 4.

Reduction of Pb_3O_4.



In order more accurately to determine the first stages of the reaction, a much larger quantity of triplumbic tetroxide was employed, and hence a greater number of points in the portion of the curve denoting the reduction to lead oxide were obtained. The change in weight with the time of reduction is given below:

TABLE III.

Time in hours	0	3	6	9	12	15	20	25
Weight in grams...	10·000	9·937	9·867	9·788	9·725	9·662	9·620	9·610

When these results were plotted as a time-reduction curve, it was seen that the break occurred considerably below the point corresponding to complete reduction to lead oxide. This is due to the fact that the second phase of the reaction had already set in, namely, that lead oxide was being reduced to lead suboxides at the same time as the triplumbic tetroxide was being reduced to lead oxide. These results point to the conclusion that the rate at which triplumbic tetroxide is reduced to lead oxide is different from the velocity with which lead oxide is reduced to lead suboxide. Glaser (*loc. cit.*) points out that when lead oxide is reduced by hydrogen, the reduction to lead suboxide is faster than the reduction of the latter to metallic lead, and hence it might be expected that the triplumbic tetroxide would be rereduced faster than lead oxide under similar conditions, but the difference would not be so marked as that between lead oxide and suboxide.

Oxidation of Lead.

Berzelius stated that lead suboxide is formed when lead is oxidised at a temperature below its melting point. An attempt was made to determine the rate of oxidation of lead, it being thought possible that the time oxidation curve would show a break at the point where the lead is completely oxidised to lead suboxide and the latter begins to be oxidised to lead oxide.

For this purpose, 1·7395 grams of lead, in fine powder, prepared by reducing the oxide, were heated in a tube connected with a mercury manometer. The tube was filled with oxygen, and the progress of the reaction followed by observing the diminution of pressure. The mercury rose rapidly at first, and more slowly towards the end of the reaction, the pressure becoming constant in about 1½ hours after the commencement of the oxidation.

When the oxidation was complete, the boat containing the oxide was removed and weighed. It was found that 1·7395 grams of lead yielded 1·8650 grams of lead oxide, that is, 100 parts of lead yield 107·21 parts of lead oxide, theory requiring 107·6. When the results of the experiment were plotted on time-pressure co-ordinates, the curve was quite regular, hyperbolic in form, and showing no break.

The regularity of the curve leads to the conclusion that in an atmosphere of pure oxygen the velocity of the reaction :

$$Pb_2O + O \longrightarrow 2PbO$$

is greater than, or at least equal to, the velocity of the reaction :

$$2Pb + O \longrightarrow Pb_2O.$$

Reduction of Cadmium Oxide.

Tanatar showed (*Zeitsch. anorg. Chem.*, 1901, **27**, 432) that cadmium suboxide, Cd_4O, is obtained by the cautious ignition of cadmium oxalate in a stream of carbon dioxide. Calorimetric measurements showed that this is not a mixture of cadmium oxide and cadmium, and Tanatar concluded that the heat of formation of carbon suboxide from the oxide and metal was about 7 Cal. By ignition of the basic oxalate of cadmium, Tanatar and Levin (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 495) obtained the suboxide, Cd_2O, and they confirmed the constitution of this compound by thermochemical measurements.

The first product of the reduction of cadmium oxide would therefore be the suboxide, Cd_2O, and again if the reaction :

$$CdO \longrightarrow Cd_2O$$

proceeds at a much greater velocity than the reaction :

$$Cd_2O \longrightarrow Cd,$$

then a break should occur in the time-reduction curve of cadmium oxides at the point where the composition of the product corresponds to Cd_2O. In an experiment,* 2·000 grams of pure cadmium oxide, prepared by igniting the hydroxide, were reduced at 300° for varying times and the loss in weight observed in Table IV shows the results obtained :

TABLE IV.

Time in hours............	0	3	7	11	13½	18	21
Weight in grams	2·000	1·964	1·921	1·866	1·858	1·854	1·841

The curve in Fig. 5 shows a distinct break at the point corresponding to the change in velocity of reduction due to the completion of the reduction of cadmium oxide to the suboxide, Cd_2O, the latter subsequently being reduced to cadmium. A second break occurs in the curve, which, however, is uncertain owing to the volatility of cadmium at this temperature (300°). At the conclusion of the last reduction, hexagonal crystals of cadmium were found on the tube containing the boat.

---

* I wish to express my thanks to Professor Campbell Brown for his kindness in allowing me the use of his pure chemicals.

Reduction of Bismuth Oxide.

Tanatar (*Zeitsch. anorg. Chem.*, 1901, **27**, 437) obtained bismuth suboxide, BiO, by heating the basic oxalate of bismuth, $Bi_2O_2(C_2O_4)$, which decomposes completely into bismuth suboxide and carbon dioxide. This chemist proved the constitution of this compound, which had previously been described by Schneider (*Ann. Phys. Chem.*, 1853, [ii], **88**, 55; *J. pr. Chem.*, 1898, [ii], **58**, 562), and its existence denied by Vanino and Treubert (*Ber.*, 1898, **31**, 1113; 1899, **31**, 1072, 1099), by showing that the heat of solution of bismuth suboxide in hydrochloric acid was different from the heat of solution of a mixture of bismuth oxide and bismuth having the same composition. From these measurements, Tanatar concludes that the heat of formation of 3 molecules of bismuth suboxide from 1 molecule each of bismuth oxide and bismuth is 11·814 Cal. The measurements of the rate of

FIG. 5.

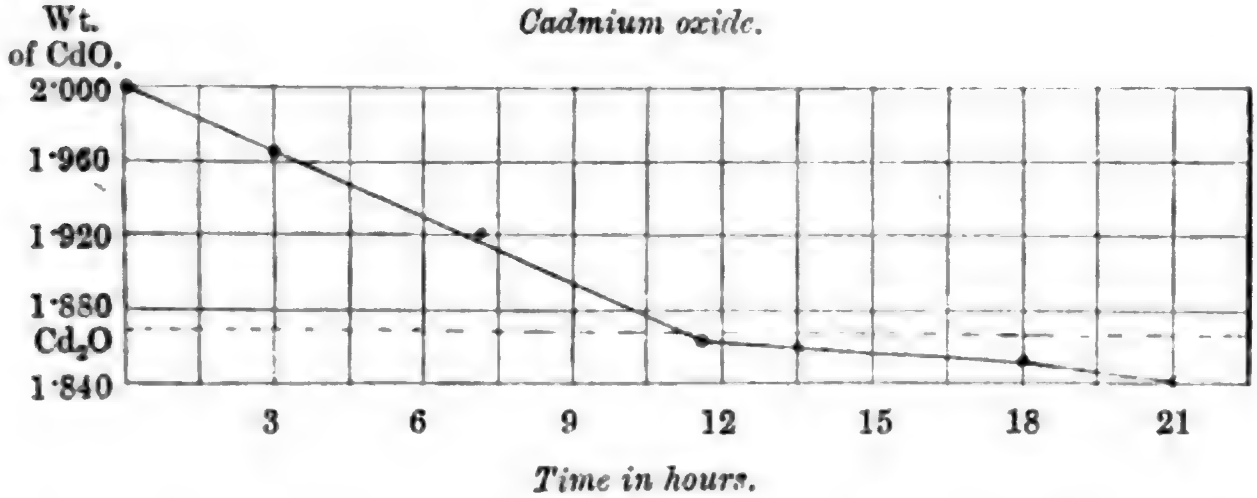
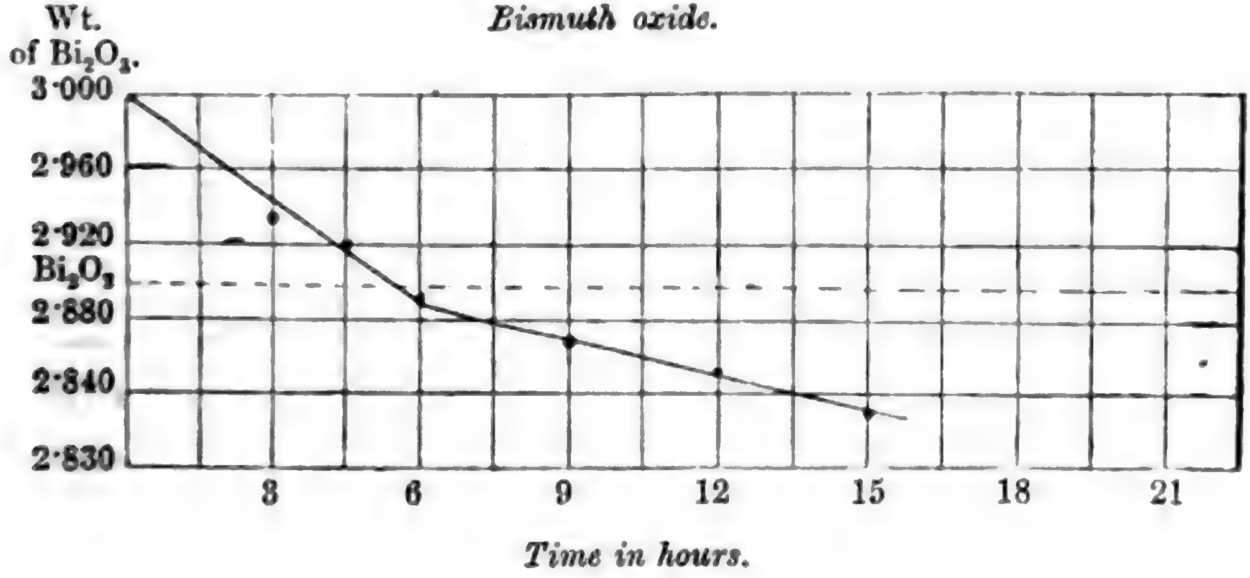


FIG. 6.



reduction of bismuth oxide in carbon monoxide show a break in the time-reduction curve very close to the point of completion of the reaction:

$$Bi_2O_3 \longrightarrow 2BiO.$$

The results are given in table V.

TABLE V.

Time in hours	0	3	4½	6	9	12	15
Weight in grams	3·000	2·934	2·920	2·890	·868	2·850	2·831

The curve corresponding to these results is shown in Fig. 6. The break in the curve occurs very near the point at which the composition of the reduction-product corresponds to bismuth suboxide.

Conclusions.

The experiments made on the velocity of reduction of the oxides of lead, cadmium, and bismuth confirm Tanatar's observations that the suboxides of these metals exist, but neither his researches nor the foregoing experiments show under what conditions these intermediate suboxides are constantly stable. When the oxides of lead, cadmium, and bismuth are reduced by carbon monoxide, the suboxides of these metals are formed as an intermediate phase in the reduction. The observation of Tanatar (*loc. cit.*), that lead suboxide decomposes into a mixture of lead and lead oxide when exposed to a moderately high temperature, indicates either that the lead suboxide is an unstable compound tending to pass into two stable substances:

$$Pb_2O \longrightarrow Pb + PbO,$$

and that with rise of temperature the velocity of this change is increased, or else that there is a definite transition-point existing at a particular temperature. These points are under investigation at present.

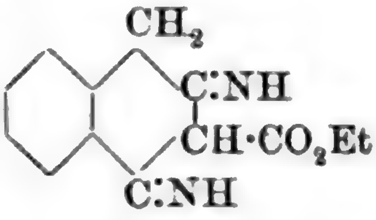
In conclusion, I wish to express my best thanks to Professor Donnan for his kind interest and advice during the course of this research.

MUSPRATT LABORATORY OF PHYSICAL AND ELECTRO-CHEMISTRY,
UNIVERSITY OF LIVERPOOL.

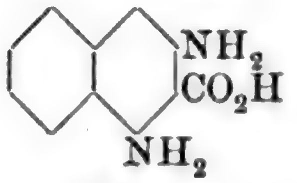
XVII.—*The Formation and Reactions of Imino-Compounds. Part VI. The Formation of Derivatives of Hydrindene from* o-*Phenylenediacetonitrile.*

By Charles Watson Moore and Jocelyn Field Thorpe.

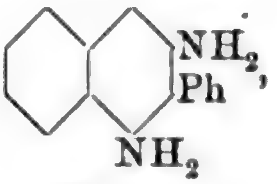
In a former communication (Trans., 1906, **89**, 1916) attention was drawn to the influence which different groups attached to the carbon atom adjacent to the carbimino-group in an imino-compound exercised on the stable form of this group, and it was mentioned that whereas ethyl 1 : 3-naphthylenediamine-2-carboxylate (I) evidently has the imino-structure, yet when the carbethoxyl group is replaced by carboxyl or by phenyl as in 1 : 3-naphthylenediamine-3-carboxylic acid (II) or 2-phenyl-1 : 3-naphthylenediamine (III):



(I.)



(II.)

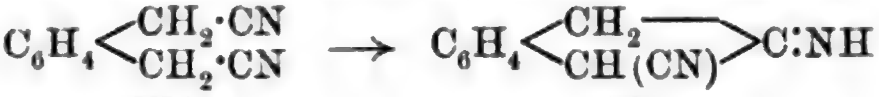


(III.)

the stable form of the compound evidently has the amino-structure.

In the present communication, we deal with a series of imino-compounds in which this influence is very much more clearly defined and in which the nature of the groups attached to the carbon atom adjacent to the carbimino-group materially affects the structure of the compound.

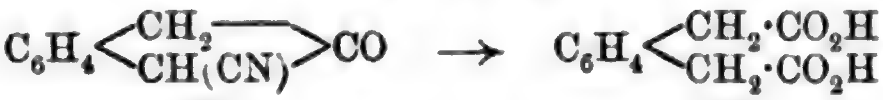
The first member of this series of imino-compounds is β-imino-α-cyanohydrindene (V), which we find can be prepared in quantitative yields when *o*-phenylenediacetonitrile (IV) is warmed in alcoholic solution in the presence of a trace of sodium ethoxide:



$$C_6H_4\left<\begin{matrix}CH_2\cdot CN\\ CH_2\cdot CN\end{matrix}\right. \rightarrow C_6H_4\left<\begin{matrix}CH_2\\ CH(CN)\end{matrix}\right>C{:}NH$$

(IV.) (V.)

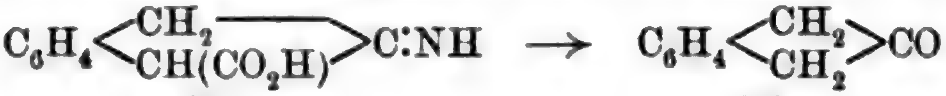
The proof of the constitution of this substance is derived from the nature of the products formed from it on hydrolysis. Thus with dilute hydrochloric acid it is hydrolysed at once, forming α-cyano-β-hydrindone (VI), from which, on treatment with caustic alkalis, *o*-phenylenediacetic acid (VII) can be readily obtained:



$$C_6H_4\left<\begin{matrix}CH_2\\ CH(CN)\end{matrix}\right>CO \rightarrow C_6H_4\left<\begin{matrix}CH_2\cdot CO_2H\\ CH_2\cdot CO_2H\end{matrix}\right.$$

(VI.) (VII.)

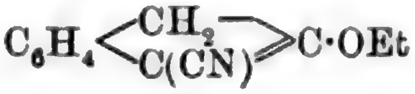
Moreover, β-imino-α-cyanohydrindene can be hydrolysed to the corresponding acid (VIII), which is readily transformed by a method described in the experimental portion into β-hydrindone (IX):



$$C_6H_4{<}\begin{array}{l}CH_2\\CH(CO_2H)\end{array}{>}C{:}NH \rightarrow C_6H_4{<}\begin{array}{l}CH_2\\CH_2\end{array}{>}CO$$

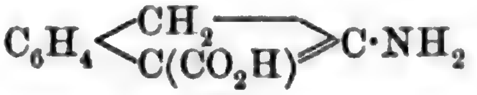
(VIII.) (IX.)

There can be no doubt that the stable form of β-imino-α-cyanohydrindene (V) has the imino-structure. It is a neutral substance which does not exhibit the slightest tendency to combine with acids; moreover, it is readily hydrolysed by dilute mineral acids to the corresponding oxygen derivative (VI). Again, when treated with ethyl alcohol and sulphuric acid, it quickly undergoes alcoholysis and is transformed into a substance which is evidently, for reasons which will be given later, 3-cyano-2-ethoxyindene (X):



$$C_6H_4{<}\begin{array}{l}CH_2\\C(CN)\end{array}{\geqslant}C{\cdot}OEt$$

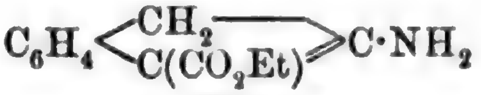
(X.)



$$C_6H_4{<}\begin{array}{l}CH_2\\C(CO_2H)\end{array}{\geqslant}C{\cdot}NH_2$$

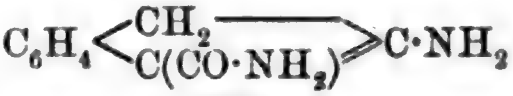
(XI.)

All these reactions are characteristic of the imino-group; if, however, the nitrile group in β-imino-α-cyanohydrindene is replaced by the carboxyl, carbethoxyl, or carboxyamino-groups, the structure of the molecule is at once changed, and there can be no doubt that these compounds are 2-aminoindene-3-carboxylic acid (XI), ethyl 2-aminoindene-3-carboxylate (XII), and 2-aminoindene-3-carboxyamide (XIII) respectively:



$$C_6H_4{<}\begin{array}{l}CH_2\\C(CO_2Et)\end{array}{\geqslant}C{\cdot}NH_2$$

(XII.)



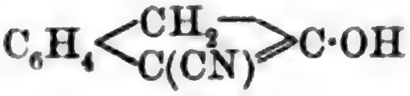
$$C_6H_4{<}\begin{array}{l}CH_2\\C(CO{\cdot}NH_2)\end{array}{\geqslant}C{\cdot}NH_2$$

(XIII.)

The proof of this is as follows: 2-aminoindene-3-carboxylic acid readily forms a salt with concentrated hydrochloric acid which is stable in the presence of the strong mineral acid but is dissociated by water. When boiled with dilute hydrochloric acid, the carboxylic acid is not hydrolysed to the corresponding oxygen derivative, but remains unacted on until carbon dioxide is eliminated, when hydrolysis at once ensues and β-hydrindone is formed. When the acid is boiled for some time with ethyl alcohol and sulphuric acid, the nitrogen group is not eliminated, but etherification alone takes place and ethyl 2-aminoindene-3-carboxylate (XII) is produced. Prolonged boiling with the above reagents fails to produce any change in the nature of the product. When the acid is treated in concentrated hydrochloric acid with nitrous acid, the whole of the nitrogen corresponding with the amino-group is eliminated in the free condition; owing, however, to the formation of ill-defined by-products, we were unable to isolate 2-hydroxyindene-3-carboxylic acid by means of this reaction. Ethyl 2-aminoindene-3-carboxylate (XII) also forms a well-defined salt with hydrochloric acid which is stable in the presence of strong hydrochloric acid but is dissociated by water. When boiled with dilute hydrochloric acid it is hydrolysed to the corresponding acid (XI), but the nitrogen group is not eliminated. When a solution of the ethyl salt in concentrated hydrochloric acid is treated with nitrous acid, the whole of the nitrogen corresponding with the amino-group is evolved in the elemental form, although in this case also the production of complex by-products rendered it impossible for us to isolate ethyl 2-hydroxyindene-3-carboxylate. It is probable that in both these reactions with nitrous acid the hydrogen atoms attached to the α-carbon atom also take part and lead to the formation of compounds of higher molecular complexity; unfortunately, it is impossible to avoid the use of excess of nitrous acid, since the whole of the aminic nitrogen is not evolved when the theoretical quantity is used.

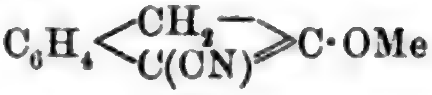
All the above reactions clearly indicate, therefore, that ethyl 2-aminoindene-3-carboxylate and 2-aminoindene-3-carboxylic acid possess an entirely different structure from β-imino-α-cyanohydrindene, and that in the first cases the aminic structure is stable and in the other the iminic. The same difference is also shown by 2-aminoindene-3-carboxyamide (XIII), which forms a salt with hydrochloric acid and is hydrolysed by dilute mineral acids to 2-aminoindene-3-carboxylic acid, the amino-group remaining unaltered.

The reactions of the oxygen derivative (α-cyano-β-hydrindone) also indicate that very slight changes in the experimental conditions employed cause it to react in either the ketonic or enolic form. α-Cyano-β-hydrindone (VI) reacts as a true acid, that is, as 3-cyano-2-hydroxyindene (XIV), since it is not only readily soluble in aqueous solution of caustic alkalis and of alkaline carbonates, but is quickly etherified by alkyl sulphates. The salts thus produced are true *O*-derivatives, since on hydrolysis they are rapidly reconverted into the ketone. Thus, when the ketone is treated with methyl sulphate, it is converted into 3-cyano-2-methoxyindene (XV):



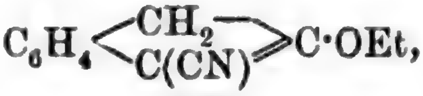
$C_6H_4{<}\begin{matrix}CH_2-\\C(CN)\end{matrix}{>}C\cdot OH$

(XIV.)



$C_6H_4{<}\begin{matrix}CH_2-\\C(CN)\end{matrix}{>}C\cdot OMe$

(XV.)

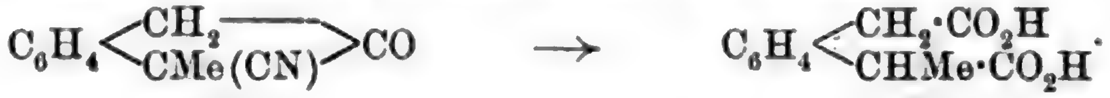


$C_6H_4{<}\begin{matrix}CH_2-\\C(CN)\end{matrix}{>}C\cdot OEt,$

(XVI.)

and, when treated with ethyl alcohol and sulphuric acid, is transformed into 3-cyano-2-ethoxyindene (XVI). Both these compounds are true *O*-salts, since, on boiling for a short time with dilute hydrochloric acid, they are hydrolysed, forming the alcohol and α-cyano-β-hydrindone. The capacity of the ketone to react in the enolic form is also shown by the fact that it gives an *O*-benzoyl derivative by the Baumann-Schotten method.

On the other hand, α-cyano-β-hydrindone reacts as a true ketone in that it forms a well-defined phenylhydrazone, and, when methylated with sodium methoxide and methyl iodide, leads to the formation of the *C*-methyl derivative, α-cyano-α-methyl-β-hydrindone (XVII):



$$C_6H_4{<}\begin{matrix}CH_2\\CMe(CN)\end{matrix}{>}CO \quad \longrightarrow \quad C_6H_4{<}\begin{matrix}CH_2\cdot CO_2H\\CHMe\cdot CO_2H\end{matrix}.$$

(XVII.) (XVIII.)

Unfortunately for the purposes of direct comparison, we have been unable to obtain this compound in a solid condition. It is a liquid which boils at 187° (25 mm.), that is to say, 8° lower than the *O*-methyl derivative, which boils at 195° (25 mm.). Its constitution is clearly proved by the fact that, on hydrolysis with alcoholic potash, it is completely transformed into *o*-phenyleneaceticpropionic acid (XVIII), and its ketonic nature is also shown by the formation of a well-defined phenylhydrazone with phenylhydrazine.

The formation of the *C*-methyl derivative in the above reaction is complete, and no trace of the *O*-methyl derivative could be detected accompanying it. It is therefore remarkable that ethylation with sodium ethoxide and ethyl iodide in ethyl-alcoholic solution should lead to the formation of the *O*-ethyl derivative, 3-cyano-2-ethoxyindene (XVI), and that none of the *C*-ethyl derivative could be isolated from the product. The compound formed in this reaction is identical with that which is derived from α-cyano-β-hydrindone on treatment with ethyl alcohol and sulphuric acid, since it not only possesses the same melting point and crystalline form as this substance, but on hydrolysis is readily transformed into ethyl alcohol and α-cyano-β-hydrindone. Several experiments were tried with the hope of inducing the ethyl group to enter at the carbon atom, but without success. For example, it was found that the sodium salt of α-cyano-β-hydrindone was very insoluble in both methyl and ethyl alcohol, and it was thought that the formation of the *O*-derivative from the sodium salt and ethyl iodide might have been due to a "constrained reaction" (compare Wislicenus, *Ahrens-Sammlung*, 1897, 249), but on treating the very soluble potassium salt with ethyl iodide under the same conditions, precisely the same result was obtained, and the *O*-ethyl derivative was the sole product formed. Moreover, when the sparingly soluble sodium salt of the ketone was treated with methyl iodide the *C*-methyl derivative was alone formed, and no trace of the *O*-methyl derivative could be isolated.

It is difficult to account for this remarkable difference in behaviour unless it is assumed that it constitutes an instance of steric hindrance, and that the spacial relations of the atoms do not permit of groups of more than a certain size attaching themselves to the α-carbon atom. Arguing on this assumption, it would seem to supply an explanation for the remarkable fact that such dissimilar groups as carboxyl and carbethoxyl bring about the same change in the molecule of β-iminohydrindene, and cause the compound to react in the amino-form.

Reviewing the evidence in this light, it will be seen that the following groups, when attached to the α-carbon atom of β-hydrindone or its imino-derivative, render the single bond between the α- and β-carbon atoms stable or unstable:

Stable.		Unstable.	
H	CN	H	$CO{\cdot}NH_2$
Me	CN	H	CO_2H
		Et	CN
		H	CO_2Et

Arguing on the assumption that it is the molecular weights or a function of the molecular weights of the groups in the second list which render it impossible for them to attach themselves to the α-carbon atom, it will be seen that the limit of stability is probably reached with the groups Me and CN, since the molecular weight of these groups (41) is only four units less than of the groups H and $CO{\cdot}NH_2$ (45). Experiments are now in progress which it is hoped will throw further light on this point, for if the above view is correct, then the alkylation of β-hydrindone will take place at the carbon atom until an alkyl group such as butyl is introduced, when alkylation will take place at the oxygen.

It should be mentioned that, although when the groups H and CN are attached to the α-carbon atom as in β-imino-α-cyanohydrindene and α-cyano-β-hydrindone the compound reacts both as a ketone and hydroxy-derivative or as an amine or imine, yet, when the aminic structure is stable, as in ethyl 2-aminoindene-3-carboxylate, 2-aminoindene-3-carboxylic acid and 2-aminoindene-3-carboxyamide, there is not the slightest evidence that they can react in the iminic form, and it is highly improbable that these compounds are capable of exhibiting tautomerism.

It may also be mentioned that the name steric hindrance is hardly a satisfactory term to apply to a phenomenon of this type, since hindrance implies merely temporary opposition. There are, however, many cases, such as, for example, the non-formation of tetraphenylmethane, in which the formation of the compound is not merely hindered but inhibited by steric conditions. To these reactions, of which we believe the experiments described in the present paper are instances, the term steric inhibition would be better applied.

β-Imino-α-cyanohydrindene does not form a sodium derivative with sodium ethoxide, and cannot, therefore, be alkylated by this means.

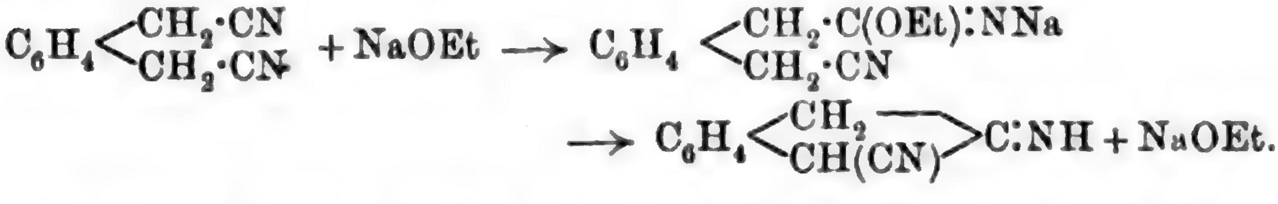
The fact is interesting because it has been shown (Trans., 1906, **89**, 1912) that ethyl β-imino-α-cyano-γ-phenylbutyrate,

$$PhCH_2{}^{*}\cdot C({:}NH)\cdot CH(CN)\cdot CO_2Et,$$

is alkylated with great difficulty, and that only after several treatments with sodium ethoxide and an alkyl iodide can one of the hydrogen atoms marked (*) be replaced by alkyl. It is evident, therefore, that ring formation in the ortho-position entirely destroys the capacity of the methylene group adjacent to the imino-group for forming a sodium derivative. The question therefore arises, what is the mechanism of the reaction by which β-imino-α-cyanohydrindene is formed from *o*-phenylenediacetonitrile? The formation is, as has been already mentioned, quantitative, and takes place with remarkable ease in the presence of a trace of sodium ethoxide. The actual quantity of sodium ethoxide which is sufficient and the rate of the reaction have not as yet been determined, but Mr. A. Holt, jun., has signified his intention of working out these questions in the near future. For the purposes of the preparation it was found that 0·1 gram of sodium ethoxide would convert 10 grams of *o*-phenylenediacetonitrile into 10 grams of β-imino-α-cyanohydrindene in the course of one hour at 80°.

Moreover, the presence of sodium ethoxide is essential to the formation of the hydrindene derivative, since, when an attempt was made to produce it by E. v. Meyer's method for preparing imino-nitriles, that is by treating a solution of the dinitrile in ether with metallic sodium, no trace could be isolated when the ether had been previously carefully freed from the last traces of alcohol, although when very small quantities of alcohol were added to the ether the formation readily took place.

The reaction is, we consider, an instance of true catalysis in which sodium ethoxide plays the part of a catalyst probably in accordance with the scheme

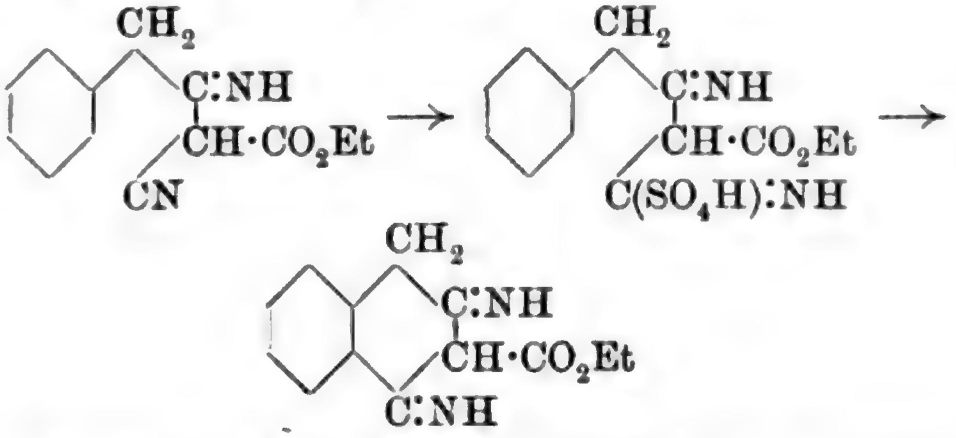


$$C_6H_4{<}\begin{matrix}CH_2\cdot CN\\ CH_2\cdot CN\end{matrix} + NaOEt \longrightarrow C_6H_4{<}\begin{matrix}CH_2\cdot C(OEt){:}NNa\\ CH_2\cdot CN\end{matrix}$$
$$\longrightarrow C_6H_4{<}\begin{matrix}CH_2\\ CH(CN)\end{matrix}{>}C{:}NH + NaOEt.$$

Attempts made to isolate the intermediate imino-ether have so far been unsuccessful because, even at low temperatures, the elimination of alcohol takes place at once with the formation of the hydrindene ring; it is probable that its existence is only momentary.

It has always seemed likely to us that the formation of imino-nitriles could be better represented by a catalytic action such as the above rather than by the equation previously suggested (Trans., 1906, **89**, 1906), but no direct evidence could be obtained on this point because the imino-nitriles prepared by us up to the present have all been capable of reacting with sodium ethoxide to form a sodium derivative, and hence the catalyst in these cases has been rapidly destroyed. It is proposed to institute experiments with the object of ascertaining whether imino-nitriles which do not react with sodium ethoxide can be formed by the action of sodium on a solution of the nitrile in ether which has been entirely freed from alcohol, and it is also hoped that by the aid of the above reaction with sodium ethoxide valuable evidence concerning ring formation will be obtained by the production of alicyclic compounds from straight chain dinitriles.

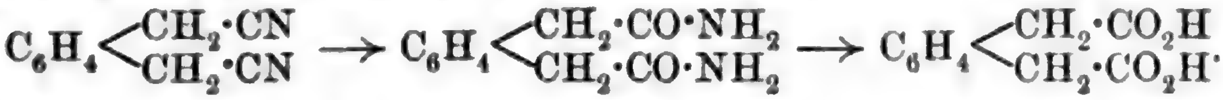
In a former communication (Trans., 1907, **91**, 584), it was suggested that the formation of ethyl 1:3-naphthylenediamine-2-carboxylate from ethyl β-imino-α-cyano-γ-phenylbutyrate by the action of cold concentrated sulphuric acid could be best explained on the assumption that the nitrile first formed an additive product with one molecule of sulphuric acid, and that sulphuric acid was then eliminated from the hydrogen atom in the ortho-position in the benzene ring; the naphthalene derivative being formed thus:



It was also mentioned that in all probability the explanation of the formation of an acid amide by dissolving a nitrile in concentrated sulphuric acid and pouring the product into water is of the same kind:

$$R\cdot CN + H_2SO_4 \longrightarrow R\cdot C(SO_4H){:}NH \longrightarrow R\cdot C(OH){:}NH \text{ or } R\cdot CO\cdot NH_2.$$

A good instance of the formation of an amide in this way is given in the present paper, for when *o*-phenylenediacetonitrile is dissolved in concentrated sulphuric acid and the product is poured into water, the amide is produced in almost quantitative yield:



$$C_6H_4{<}\begin{matrix}CH_2\cdot CN\\ CH_2\cdot CN\end{matrix} \longrightarrow C_6H_4{<}\begin{matrix}CH_2\cdot CO\cdot NH_2\\ CH_2\cdot CO\cdot NH_2\end{matrix} \longrightarrow C_6H_4{<}\begin{matrix}CH_2\cdot CO_2H\\ CH_2\cdot CO_2H\end{matrix}$$

Since the amide is completely converted into *o*-phenylenediacetic acid on warming with potash, this method is probably the best for preparing this acid in quantity.

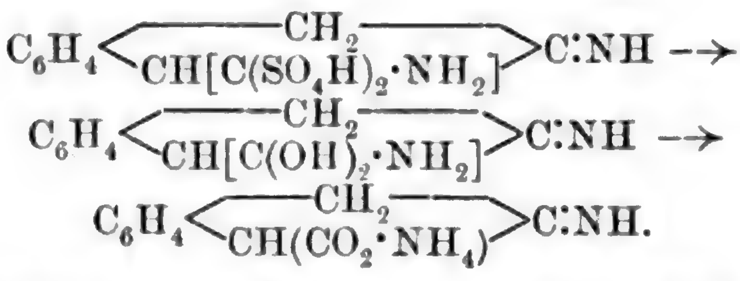
During a conversation with Dr. F. E. Matthews on this subject, he mentioned that his experiments with certain nitriles pointed to the formation of an additive product from one molecule of the nitrile and two of sulphuric acid, but at that time the compounds investigated by us furnished no evidence of the formation of this double additive product, for although the formation of the amide could be readily explained by its means:

$$R\cdot CN + 2H_2SO_4 \longrightarrow R\cdot C(SO_4H)_2\cdot NH_2 \longrightarrow R\cdot C(OH)_2\cdot NH_2 \longrightarrow R\cdot CO\cdot NH_2 + H_2O,$$

yet it was difficult to see how the formation of an additive product of this kind could lead to the production of the naphthalene ring in the manner described above.

β-Imino-α-cyanohydrindene is, however, a compound which without doubt forms an additive product with two molecules of sulphuric acid, and we are indebted to Dr. Matthews for a suggestion which has enabled us to explain the curious behaviour of this imino-nitrile with concentrated sulphuric acid.

For some time considerable difficulty was experienced in hydrolysing the nitrile group of β-imino-α-cyanohydrindene without either breaking the hydrindene ring or causing the formation of products of higher molecular weight. As already stated, the imino-nitrile is readily hydrolysed by dilute mineral acids, forming α-cyano-β-hydrindone, but when the action of the hydrolysing agent is prolonged, the ketone condenses with itself and a derivative of bishydrindene is formed. When either the ketone or the imino-compound is treated with alkaline hydrolysing agents, the disruption of the indene ring is rapidly effected and *o*-phenylenediacetic acid is the sole product. An attempt was therefore made to prepare the amide from β-imino-α-cyanohydrindene by dissolving it in concentrated sulphuric acid and pouring the product into water. It was found that the imino-nitrile readily reacted with the strong acid, and that after leaving for half an hour a clear solution could be obtained on pouring a test portion into water. The sulphuric acid solution was therefore poured on ice, when the solid which separated was found to consist almost entirely of the carboxylic acid and to contain only a small quantity (about 2 per cent.) of the amide. We consider that the formation of the acid in this manner is due to the production of an additive product of the imino-nitrile with two molecules of sulphuric acid which subsequently reacts with water, forming the ammonium salt of the acid, thus:



$$C_6H_4\left\langle\begin{array}{c}CH_2\\ CH[C(SO_4H)_2\cdot NH_2]\end{array}\right\rangle C{:}NH \longrightarrow$$
$$C_6H_4\left\langle\begin{array}{c}CH_2\\ CH[C(OH)_2\cdot NH_2]\end{array}\right\rangle C{:}NH \longrightarrow$$
$$C_6H_4\left\langle\begin{array}{c}CH_2\\ CH(CO_2\cdot NH_4)\end{array}\right\rangle C{:}NH.$$

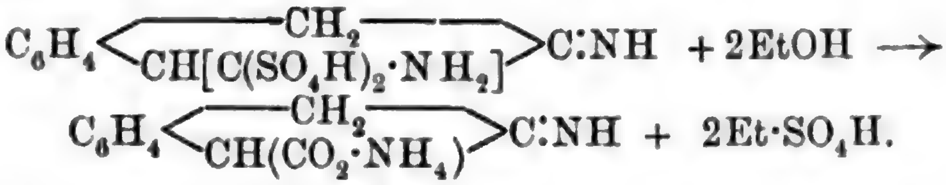
---

* These formulæ are written in the iminic form for the sake of clearness. The compounds, of course, have the aminic structure.

This ammonium salt is then at once decomposed by the free sulphuric acid present, yielding the free carboxylic acid.

It is, of course, evident that the product formed by water on the sulphuric acid additive product may either pass by rearrangement into the ammonium salt or may eliminate water and pass into the amide, and it is possible that the small quantity of amide produced in the above reaction may have been formed in this way, but for certain reasons we are inclined to think that its formation is due to the partial production of a mono-additive product which reacts with water in the manner just indicated. There is at present no direct evidence for this, but it is rendered probable, because if the time during which the action of concentrated sulphuric acid is continued is less than that mentioned above, a larger mount of the amide is formed. It is reasonable to suppose that the formation of a mono-additive product in every case precedes the formation of the di-additive product.

When the concentrated sulphuric acid solution of the imino-nitrile is poured into well-cooled absolute alcohol, the product is the same as with water, ethyl hydrogen sulphate being produced in accordance with the scheme:

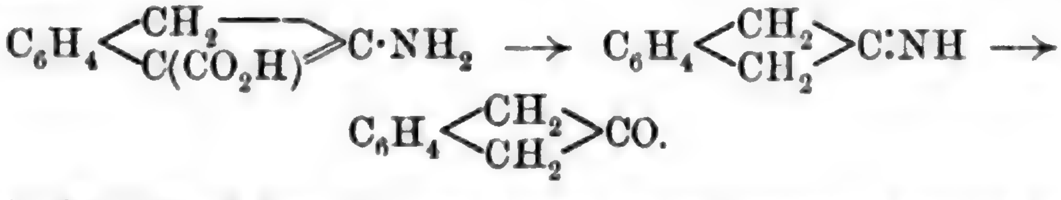


$$C_6H_4{<}\begin{matrix}CH_2\\CH[C(SO_4H)_2\cdot NH_2]\end{matrix}{>}C{:}NH + 2EtOH \longrightarrow$$

$$C_6H_4{<}\begin{matrix}CH_2\\CH(CO_2\cdot NH_4)\end{matrix}{>}C{:}NH + 2Et\cdot SO_4H.$$

No trace of the ethyl salt of the carboxylic acid is formed in this reaction, and in order to produce this substance the ethyl-alcoholic solution containing ethyl hydrogen sulphate must be heated for some considerable time on the water-bath.

As already mentioned, 2-aminoindene-3-carboxylic acid passes into β-hydrindone on distilling a solution of it in dilute sulphuric acid with steam:



$$C_6H_4{<}\begin{matrix}CH_2\\C(CO_2H)\end{matrix}{>}C\cdot NH_2 \longrightarrow C_6H_4{<}\begin{matrix}CH_2\\CH_2\end{matrix}{>}C{:}NH \longrightarrow$$

$$C_6H_4{<}\begin{matrix}CH_2\\CH_2\end{matrix}{>}CO.$$

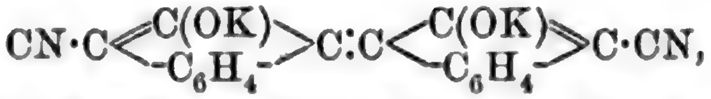
The hydrolysis of the nitrogen group takes places as soon as and not until carbon dioxide is eliminated, and it is therefore probable that β-iminohydrindene (XIX) is a true imino-compound. Unfortunately, we have been unable to isolate this substance, for when the reactions which should give it, such as the elimination of carbon dioxide from the carboxylic acid by heat, are tried, only compounds formed by intramolecular condensation are produced. But that it is a true imino-compound readily hydrolysable by acids can be inferred by the production of β-hydrindone from β-nitroindene, which, as Wallach has shown (*Annalen*, 1904, **336**, 1), can be effected by reduction and hydrolysis.

β-Hydrindone has been prepared by Schad (*Ber.*, 1893, **26**, 222) and Benedikt (*Annalen*, 1893, **275**, 353) by the distillation of the calcium salt of *o*-phenylenediacetic acid; by Heusler and Schieffer (*Ber.*, 1899, **32**, 30) from the indene of coal-tar, and more recently by Wallach in the manner mentioned above. It is described as a white, crystalline substance which rapidly changes on exposure to the air to a brown resin. β-Hydrindone prepared by our method exhibits no tendency to decompose, and has been kept for many months without showing any signs of change. It is probable, therefore, that by our method of preparation some impurity has been removed which always accompanied β-hydrindone when prepared by the methods quoted.

All the derivatives of β-hydrindone and its imide described in this paper possess one characteristic reaction in common. When a trace is added to concentrated sulphuric acid a brilliant blue solution is produced. This colour is discharged on adding a further quantity of the hydrindene derivative, but on adding the colourless solution thus formed to a further quantity of sulphuric acid, the blue colour is again produced.

It was ultimately found that when the concentrated sulphuric acid had been carefully purified no colour was produced, but that immediately a trace of an oxidising agent such as nitric acid was added it was at once formed. It is very difficult to obtain sulphuric acid which does not give this reaction, the pure commercial acid giving it to a very marked degree. When very pure sulphuric acid which has been found not to give the colour is mixed with a trace of selenic acid, the blue colour formed is very intense.

Neither the α- nor β-hydrindone has, so far as we are aware, been observed to oxidise to the double molecule analogous to the formation of indigo from indoxyl, and it is therefore of interest to note that β-imino-α-cyanohydrindene readily undergoes this transformation. When a solution of this substance in alcoholic potash is shaken in the air, it rapidly becomes intensely purple, ammonia at the same time being eliminated. On standing, the solution deposits crystals of a potassium salt of the formula:



$$\mathrm{CN{\cdot}C}\left\langle\begin{matrix}\mathrm{C(OK)}\\ \mathrm{-C_6H_4-}\end{matrix}\right\rangle\mathrm{C{:}C}\left\langle\begin{matrix}\mathrm{C(OK)}\\ \mathrm{-C_6H_4-}\end{matrix}\right\rangle\mathrm{C{\cdot}CN},$$

which dissolve in hot water, forming an intensely bluish-purple solution from which wool can be dyed a rich shade of purple. On treating the aqueous solution of the potassium salt with acids, the free hydroxyl compound is produced as a red amorphous precipitate. It is, however, insoluble in all solvents, and has not been obtained in a crystalline state.

EXPERIMENTAL.

o-*Phenylenediacetonitrile*, $C_6H_4(CH_2\cdot CN)_2$.

The preparation of ωω′-dibromo-*o*-xylene was effected in the manner described in a previous paper (Trans., 1907, **91**, 1695), and it was converted into the dinitrile by the aid of potassium cyanide in dilute alcoholic solution. The method adopted was as follows, the operation being conducted in the open air, since ωω′-dibromo-*o*-xylene has a most painful effect on the eyes. About 10 per cent. more than the theoretical quantity of potassium cyanide was dissolved in as little water as possible, and then mixed with three times its volume of ethyl alcohol. After the mixture had been raised to the boiling point, the finely-ground bromo-compound was added in small portions at a time in such a manner that the heat of the reaction kept the liquid at the boiling point. When all had been added, the mixture was allowed to stand for half an hour, when it was diluted with water, and the oil which was then precipitated extracted with ether. After drying, the ethereal extract was evaporated to a small bulk and allowed to stand, when crystals of the dinitrile slowly separated. These were collected and recrystallised from alcohol, the dark-coloured oil which was obtained on evaporating the ethereal mother-liquor yielding a further quantity of crystals on being mixed with an equal volume of alcohol. Pure *o*-phenylenediacetonitrile melts at 60°.

When *o*-phenylenediacetonitrile is recrystallised from either methyl or ethyl alcohol, but best from the former, it can be obtained in two forms, one of which separates at temperatures below 18°, the other at temperatures above this point. The modification separating at the lower temperature which consists of needles is unstable, and almost immediately passes into the stable or prismatic form. At the same time there is evidently a considerable change in volume, since each needle on passing into the prismatic form breaks up with a loud report, which, if the needles have grown to any size, is almost explosive. This property is best shown by melting about a gram of the dinitrile under light petroleum (b. p. 80—90°), in which it is almost insoluble, and then rapidly cooling below 10°. On touching, the oil will solidify in the labile form, which will almost immediately pass into the stable variety, the change being accompanied by a loud explosion, which, in one or two experiments, shattered the test tube.

Formation of o-*phenylenediacetamide* and o-*phenylenediacetic acid from* o-*phenylenediacetonitrile*.

The transformation of *o*-phenylenediacetonitrile into *o*-phenylenediacetamide may be readily effected by the aid of concentrated sulphuric acid, the following conditions being found most suitable. The dinitrile was slowly added to five times its weight of concentrated sulphuric acid, and the solution, which became warm, allowed to stand at the ordinary temperature until a test portion, on being diluted with water, showed no deposition of oil. The whole was then poured into water, and the clear solution made alkaline with ammonia, when the formation of ammonium sulphate in the solution caused the diamide to be completely precipitated. It was collected by filtration and crystallised from water, from which solvent it separated in long, silky needles, resembling asbestos, melting at 198°:

0·1532 gave 0·3501 CO_2 and 0·0889 H_2O. C = 62·30; H = 6·44.

$C_{10}H_{12}O_2N_2$ requires C = 62·5; H = 6·2 per cent.

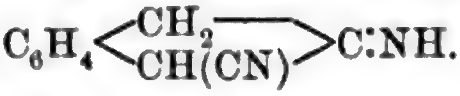
o-*Phenylenediacetamide* is very sparingly soluble in alcohol, and is readily hydrolysed by aqueous solutions of caustic alkalis. It was completely converted into *o*-phenylenediacetic acid by boiling with excess of caustic potash solution until the evolution of ammonia had ceased, and then acidifying the solution with hydrochloric acid. The acid was extracted by ether, the ethereal extract dried and evaporated, the residue, which solidified on cooling, being crystallised from water. *o*-Phenylenediacetic acid prepared in this way showed the correct melting point, namely, 150°:

0·2012 gave 0·4553 CO_2 and 0·0905 H_2O. C = 61·70; H = 4·99.

$C_{10}H_{10}O_4$ requires C = 61·8; H = 5·1 per cent.

The yield of the acid from *o*-phenylenediacetonitrile by this process is 90 per cent. of the theory.

β-Imino-α-cyanohydrindene,



$C_6H_4{<}\begin{matrix}CH_2\text{———}\\CH(CN)\end{matrix}{>}C{:}NH.$

In order to prepare this substance, 10 grams of *o*-phenylenediacetonitrile were dissolved in 40 c.c. of ethyl alcohol and introduced into a flask fitted with a reflux condenser, the apparatus being so devised that a current of dry hydrogen could be driven through the flask throughout the operation. The alcoholic solution was then heated to boiling on the water-bath, and 1 c.c. of a solution of one gram of sodium dissolved in 10 c.c. of alcohol added through the condenser. On adding the sodium ethoxide the solution became at once yellow, the yellow colour increasing in intensity as the reaction progressed. After one hour of gentle boiling, the contents of the flask were allowed to cool, when yellow prisms separated which were collected, washed and dried. The compound prepared in this way was almost pure, the yield being practically quantitative. It was purified for analysis by recrystallisation from hot alcohol, from which solvent it separated in prisms, usually slightly yellow, which melted at 193°:

0·1548 gave 0·4381 CO_2 and 0·0718 H_2O. C = 77·18; H = 5·15.
0·2072 „ 31·8 c.c. of nitrogen at 18° and 757 mm. N = 17·67.
$C_{10}H_8N_2$ requires C = 76·9; H = 5·1; N = 17·9 per cent.

The yellow colour of *β-imino-a-cyanohydrindene* is evidently due to the presence of traces of impurity, since on repeated crystallisation it can be obtained almost colourless. The imino-nitrile sublimes when heated, and does not form a sodium compound with sodium ethoxide. It is readily soluble in hot alcohol, sparingly so in cold alcohol or benzene, and practically insoluble in water. Its alcoholic solution gives no colour with ferric chloride, but when a small quantity of the solid is dissolved in concentrated sulphuric acid containing a trace of an oxidising agent, a fine blue coloration is produced. This reaction is best seen with sulphuric acid containing a trace of selenic acid. Indeed, it is a matter of some difficulty to obtain sulphuric acid which does not give this reaction. Ordinary sulphuric acid gives it at once, and even after careful distillation a faint colour is produced.

The *phenylhydrazone.*—β-Imino-a-cyanohydrindene reacts slowly when boiled in acetic acid solution with phenylhydrazine acetate, and, on cooling, yellow crystals are deposited which when crystallised from alcohol yield pale yellow plates which melt and decompose at 187°:

0·1643 gave 24·2 c.c. of nitrogen at 16° and 762 mm. N = 17·21.
$C_{16}H_{13}N_3$ requires N = 17·0 per cent.

This compound is evidently the same as that produced by the action of phenylhydrazine on a-cyano-β-hydrindone (see later).

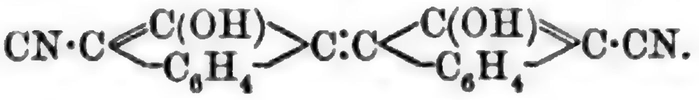
Conversion of β-imino-a-cyanohydrindene into 3-*cyano*-2-*ethoxyindene.*

This conversion was effected by dissolving the imino-compound in ethyl alcohol, adding one-third of the volume of concentrated sulphuric acid, and, after boiling the solution on the water-bath for twenty minutes, allowing it to stand for twelve hours. At the end of this time the product was poured into water, the solid then formed filtered and crystallised from alcohol. In this way, colourless needles were obtained melting at 84°:

0·2636 gave 0·7516 CO_2 and 0·1450 H_2O. C = 77·76; H = 6·1.
0·2090 „ 14·3 c.c. of nitrogen at 14° and 746 mm. N = 7·9.
$C_{12}H_{11}ON$ requires C = 77·8; H = 5·9; N = 7·6 per cent.

This compound is evidently the same as that produced by the ethylation of a-cyano-β-hydrindone (see later).

Bis-1-*cyano*-2-*hydroxyindene.*



$$\mathrm{CN{\cdot}C}{<}\begin{matrix}\mathrm{C(OH)}\\ \mathrm{C_6H_4}\end{matrix}{>}\mathrm{C{:}C}{<}\begin{matrix}\mathrm{C(OH)}\\ \mathrm{C_6H_4}\end{matrix}{>}\mathrm{C{\cdot}CN}.$$

The oxidation of β-imino-α-cyanohydrindene to the potassium salt of the above substance was effected in the following way: Five grams of the imino-compound were dissolved in alcohol containing rather more than one equivalent of potash. After the solution had been warmed to 50°, air was drawn through it until a test portion, on dilution with water, gave no precipitate of unchanged imino-compound. The deep purple solution was allowed to stand, when crystals of the *potassium* salt slowly separated. These were collected, washed with cold water and dried, yielding slender, deep blue needles with faint copper reflex:

0·2471 gave 0·1112 K_2SO_4. K = 20·12.

$C_{20}H_8O_2N_2K_2$ requires K = 20·20 per cent.

The potassium salt is insoluble in cold water, but readily dissolves on boiling. The deep purple solution thus obtained deposits the crystalline salt completely on cooling, but in hot solution can be used for the purpose of dyeing wool. The *ammonium* and *sodium* salts show a greater degree of solubility in water.

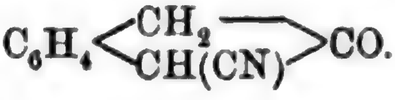
The free *acid* is deposited as a red, amorphous precipitate on adding hydrochloric acid to a solution of the above potassium salt. It is insoluble in all the usual solvents, and therefore for the purposes of analysis the precipitated acid was washed and dried:

0·2317 gave 0·6560 CO_2 and 0·0690 H_2O. C = 77·22; H = 3·31.

$C_{20}H_{10}O_2N_2$ requires C = 77·4; H = 3·2 per cent.

When heated the compound partly sublimes, but for the most part chars without melting. It is readily soluble in alkali carbonates and caustic alkalis, forming the highly coloured alkali salts just described.

α-*Cyano*-β-*hydrindone*,



$$\mathrm{C_6H_4}{<}\begin{matrix}\mathrm{CH_2}\\ \mathrm{CH(CN)}\end{matrix}{>}\mathrm{CO}.$$

This substance was prepared in the following way: Ten grams of β-imino-α-cyanohydrindene were mixed with 200 c.c. of water to which 50 c.c. of concentrated hydrochloric acid had been added, and the mixture boiled until a test portion was completely soluble in dilute sodium carbonate solution, an operation which usually required from ten to fifteen minutes. The mixture was then cooled and extracted three times with ether, the yellow ethereal solution being subsequently thoroughly shaken with dilute aqueous sodium carbonate, whereby the colourless ketone was completely extracted, leaving the yellow impurities dissolved in the ether. The ketone was precipitated on adding acid to the sodium carbonate solution, and was purified by recrystallisation from dilute alcohol, when it was obtained in colourless plates melting at 172° with decomposition. The compound also crystallises well from glacial acetic acid:

0·3704 gave 1·0316 CO_2 and 0·1509 H_2O. C = 75·95; H = 4·49.
0·1990 gave 15·6 c.c. of nitrogen at 19° and 772 mm. N = 9·2.
$C_{10}H_7ON$ requires C = 76·4; H = 4·5; N = 8·9 per cent.

a-Cyano-β-hydrindone is readily soluble in alkali carbonates. When a small quantity is added to concentrated sulphuric acid containing a trace of an oxidising agent, a deep blue solution is produced similar to that formed with the imino-compound. The ketone gives a green colour with ferric chloride, but its solution in alcoholic potash does not oxidise in the air.

The *phenylhydrazone*, $C_{16}H_{13}N_3$, is formed as a yellow, crystalline precipitate on adding a solution of phenylhydrazine acetate to a solution of the ketone in glacial acetic acid and boiling. It crystallises from absolute alcohol in small needles melting at 187° with decomposition:

0·2464 gave 36·0 c.c. of nitrogen at 13° and 752 mm. N = 17·1.
$C_{16}H_{13}N_3$ requires N = 17·0 per cent.

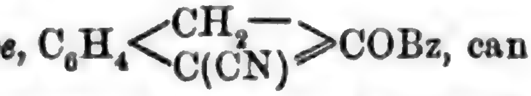
The *potassium* salt, $C_{10}H_6ONK$, is formed as a white, crystalline precipitate on adding a slight excess of alcoholic potash to a solution of the ketone in alcohol. It can be recrystallised from alcohol, from which solvent it separates in colourless plates:

0·4375 gave 0·1925 K_2SO_4. K = 19·72.
$C_{10}H_6ONK$ requires K = 20·0 per cent.

The potassium salt is readily soluble in alcohol, whereas the *sodium* salt is very sparingly soluble. The sodium salt is, moreover, much less soluble in water than the potassium salt, and is completely precipitated from its aqueous solution by excess of sodium hydroxide.

The *silver* salt, $C_{10}H_6ONAg$, is precipitated on adding the calculated quantity of silver nitrate solution to an aqueous solution of the potassium salt. It is a white powder which becomes slowly coloured on exposure to light:

0·2731 gave 0·1119 Ag. Ag = 40·97.
$C_{10}H_6ONAg$ requires Ag = 41·0 per cent.

The O-*benzoyl derivative*,  $C_6H_4{<}\begin{matrix}CH_2\text{—}\\C(CN)\end{matrix}{\geqslant}COBz$, can be prepared by dissolving the ketone in excess of potassium hydroxide solution, adding excess of benzoyl chloride and shaking until all the chloride has dissolved. The insoluble precipitate which remains, on being filtered and recrystallised from alcohol, can be obtained in slender, colourless needles melting at 123°:

0·1774 gave 0·5073 CO_2 and 0·0654 H_2O. $C = 77·99$; $H = 4·09$.
$C_{17}H_{11}O_2N$ requires $C = 78·1$; $H = 4·2$ per cent.

An intensely green compound is formed in this reaction, but since it is readily soluble in cold alcohol, the benzoyl derivative can be easily freed from it. The benzoyl derivative is quickly hydrolysed with dilute alcoholic potash, yielding α-cyano-β-hydrindone and benzoic acid.

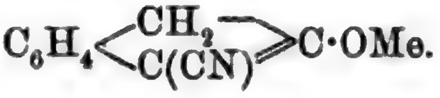
Formation of o-phenylenediacetic acid from α-cyano-β-hydrindone.

On boiling α-cyano-β-hydrindone with excess of aqueous potassium hydroxide, ammonia was slowly evolved, and after heating for twelve hours the evolution had ceased. The solution was then acidified and extracted with ether, the ethereal extract evaporated and the residue crystallised from water, when the long, characteristic needles of *o*-phenylenediacetic acid, melting at 150°, separated:

0·2236 gave 0·5056 CO_2 and 0·1007 H_2O. $C = 61·66$; $H = 5·00$.
$C_{10}H_{10}O_4$ requires $C = 61·8$; $H = 5·1$ per cent.

Alkylation of α-cyano-β-hydrindone by etherifying agents.

3-*Cyano-2-methoxyindene*,



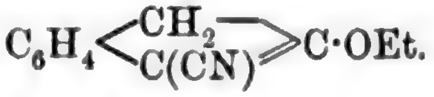
$C_6H_4\left<\begin{matrix}CH_2\text{—}\\C(CN)\end{matrix}\right>C\cdot OMe.$

In order to prepare this compound, 3 grams of the ketone were dissolved in 10 times its weight of methyl alcohol and the solution mixed with 5 grams of methyl sulphate. After being boiled for a few minutes, the solution was treated with excess of potassium hydroxide and vigorously shaken until all the excess of methyl sulphate had been destroyed, when the insoluble residue was filtered and recrystallised from methyl alcohol. The compound may also be prepared from methyl alcohol and sulphuric acid by dissolving 3 grams of the ketone in 10 times its weight of methyl alcohol, adding one-third of the volume of concentrated sulphuric acid and, after boiling, allowing to stand some hours. The methoxy-derivative then separates completely from the solution and can be collected at once by filtration. When recrystallised from methyl alcohol, 3-cyano-2-methoxyindene forms long, colourless needles melting at 88° and boiling at 195° (25 mm.):

0·2139 gave 0·6043 CO_2 and 0·1045 H_2O. $C = 77·05$; $H = 5·42$.
$C_{11}H_9ON$ requires $C = 77·2$; $H = 5·3$ per cent.

The compound also crystallises well from light petroleum (b. p. 80—90°). When boiled for a few minutes with dilute hydrochloric acid, 3-cyano-2-methoxyindene slowly passes into solution, and on cooling the solution crystals of α-cyano-β-hydrindone melting and decomposing at 172° separate. It is evident, therefore, that the compound is the *O*-methyl derivative.

3-*Cyano-2-ethoxyindene*,



$$C_6H_4{<}\begin{matrix}CH_2\text{—}\\C(CN)\end{matrix}{>}C\cdot OEt.$$

The ethoxy-derivative was prepared by the action of ethyl alcohol and sulphuric acid on α-cyano-β-hydrindone. Three grams were dissolved in 30 grams of ethyl alcohol and the solution mixed with one-third of its volume of concentrated sulphuric acid. After having been raised to the boiling point, the solution was allowed to stand, when crystals of the ethoxy-derivative slowly separated. These were collected and recrystallised from ethyl alcohol, when they were obtained in slender, colourless needles melting at 84° and boiling at 212° (25 mm.):

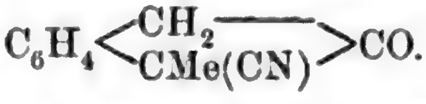
0·2451 gave 0·6990 CO_2 and 0·1349 H_2O. C = 77·78; H = 6·11.

$C_{12}H_{11}ON$ requires C = 77·8; H = 5·9 per cent.

When boiled with dilute hydrochloric acid, 3-cyano-2-ethoxyindene passes slowly into solution, and if the solution is cooled crystals of α-cyano-β-hydrindone melting and decomposing at 172° separate. Both the methoxy- and ethoxy-derivatives give the characteristic blue colour of derivatives of β-hydrindone and β-iminohydrindene with concentrated sulphuric acid containing a trace of an oxidising agent. The vapours of both compounds possess a peculiar garlic-like odour.

Alkylation of α-Cyano-β-hydrindone through the Alkali Salts with an Alkyl Iodide.

α-*Cyano*-α-*methyl*-β-*hydrindone*,



$$C_6H_4{<}\begin{matrix}CH_2\text{——}\\CMe(CN)\end{matrix}{>}CO.$$

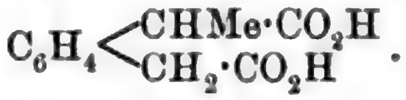
It has already been mentioned that the sodium salt of α-cyano-β-hydrindone is sparingly soluble in hot alcohol, whereas the potassium salt readily dissolves. For reasons given in the introduction, it was therefore necessary to investigate the action of methyl iodide on both the sodium and potassium salts, but since the reactions were carried out in the same way, and the products in each case were found to be identical, it is only necessary to describe one of them in detail: 3·6 grams of pure potassium hydroxide were dissolved in 100 c.c. of methyl alcohol, and the solution mixed with 10 grams of α-cyano-β-hydrindone. The clear yellow solution was then transferred to a Geissler flask, mixed with 20 grams of methyl iodide and heated on the water-bath for two hours. At the end of this time the excess of methyl iodide was removed by distillation, water added to the residue, and the oil which separated extracted by ether. The ethereal solution was then washed with water to remove alcohol, and finally with dilute aqueous sodium carbonate to remove any unchanged ketone, dried and evaporated. The oil which remained boiled at 187° (25 mm.), passing over as a viscous, colourless liquid, which could not, however, be induced to solidify:

0·2201 gave 0·6211 CO_2 and 0·1071 H_2O. C = 76·96; H = 5·40.
$C_{11}H_9ON$ requires C = 77·2; H = 5·3 per cent.

The *phenylhydrazone*, $C_{17}H_{15}N_3$, was prepared by dissolving the ketone in glacial acetic acid, adding a solution of phenylhydrazine acetate in glacial acetic acid, and boiling for a few minutes. On cooling, yellow crystals of the salt separated, which were obtained in yellow prisms, melting at 169° by recrystallisation from alcohol:

0·2179 gave 30·7 c.c. of nitrogen at 17° and 756 mm.; N = 16·26.
$C_{17}H_{15}N_3$ requires N = 16·1 per cent.

o-*Phenyleneaceticpropionic Acid*,



$$C_6H_4<\begin{matrix}CHMe\cdot CO_2H\\ CH_2\cdot CO_2H\end{matrix}.$$

The constitution of α-cyano-α-methyl-β-hydrindone was proved by the formation of the above acid on hydrolysis. The ketone was boiled in a Geissler flask with a solution of one and a half times the calculated quantity of potash dissolved in methyl alcohol until a test portion on dilution with water showed no separation of oil. Water was then added, and the solution freed from methyl alcohol by evaporation. The clear aqueous solution was then acidified and extracted with ether, the ethereal extract being free from the acid by extracting it with a little aqueous sodium carbonate. On acidifying the sodium carbonate extract, the acid was precipitated and was purified by recrystallisation from hot water, being obtained in small, colourless needles melting at 152°:

0·2011 gave 0·4665 CO_2 and 0·1067 H_2O. C = 63·27; H = 5·90.
$C_{11}H_{12}O_4$ requires C = 63·5; H = 5·8 per cent.

The acid is much less soluble in ether than *o*-phenylenediacetic acid.

3-*Cyano*-2-*ethoxyindene.*

The action of ethyl iodide on either the sodium or potassium salts of α-cyano-β-hydrindone in ethyl-alcoholic solution leads to the formation of the above *O*-ethyl derivative, although the experimental conditions were precisely the same as those which in the case of methyl iodide led to the production of the *C*-methyl derivative. Ten grams of the ketone were added to a solution of 3·6 grams of potassium hydroxide in 100 c.c. of ethyl alcohol, excess of ethyl iodide was then added and the solution heated on the water-bath for two hours. At the end of this time the excess of ethyl iodide was removed by evaporation, water added, and the resulting oil, which rapidly solidified, was extracted by ether. The ethereal extract, after being washed with water, was shaken with dilute sodium carbonate solution to remove any unchanged ketone, dried and evaporated.

The oily residue quickly became solid, and after being recrystallised from ethyl alcohol was obtained in slender, colourless needles melting at 84°:

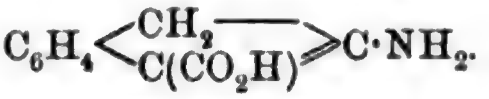
0·2094 gave 0·5980 CO_2 and 0·1155 H_2O. C = 77·8; H = 6·1.

$C_{12}H_{11}ON$ requires C = 77·8; H = 5·9 per cent.

When the compound was mixed with a specimen of 3-cyano-2-ethoxyindene prepared by the etherification of α-cyano-β-hydrindone (see page 181), no alteration in the melting point was produced, and when it was boiled for a few minutes with dilute hydrochloric acid it was completely hydrolysed to α-cyano-β-hydrindone. There could be no doubt, therefore, that it was the *O*-ethyl derivative.

Action of Concentrated Sulphuric Acid on β-Imino α-cyanohydrindene.

2-Aminoindene-3-carboxylic Acid,



$$C_6H_4{<}\begin{matrix}CH_2\text{——}\\C(CO_2H)\end{matrix}{>}C{\cdot}NH_2.$$

The formation of 2-aminoindene-3-carboxylic acid from the imino-nitrile can be readily effected by the action of concentrated sulphuric acid. Twenty grams of β-imino-α-cyanohydrindene were added gradually to 200 c.c. of concentrated sulphuric acid, with constant stirring, whereby the temperature rose to 30°. On adding the first portion of the imino-nitrile, the deep blue solution to which reference has already been made was formed. This colour disappeared on adding more of the imino-nitrile, and when all had dissolved, the solution, which was pale yellow, was left at the ordinary temperature for one hour. The strongly acid solution was then poured in a thin stream on ice, when the clear solution which was first formed gradually deposited a heavy white precipitate. The decomposition of the sulphuric acid addition product takes place, however, only slowly at 0°, and the above solution must be left for at least an hour before the decomposition is complete.

After the ice had all melted, the solution was filtered, and the insoluble residue treated with dilute sodium hydroxide solution and filtered, the insoluble portion being subsequently washed with dilute alkali in order to remove the last traces of acid. The alkaline solution, on being acidified with hydrochloric acid, gave a precipitate of the free acid which was collected and recrystallised from alcohol, when it was obtained in pale yellow needles melting and decomposing at 171°:

0·2632 gave 0·6622 CO_2 and 0·1270 H_2O. C = 68·6; H = 5·3.

$C_{10}H_9O_2N$ requires C = 68·6; H = 5·1 per cent.

The acid is soluble in hot water and can be recrystallised from this solvent, but it is advisable to use alcohol for this purpose, since at the higher temperature some carbon dioxide is always eliminated.

The compound is both an acid and a base. Thus it is readily soluble in alkali carbonates and dissolves in dilute ammonia, but the salts formed are evidently unstable, since, for example, on boiling a solution of the ammonium salt containing excess of ammonia, the free acid separates on cooling even though the solution is still alkaline to litmus.

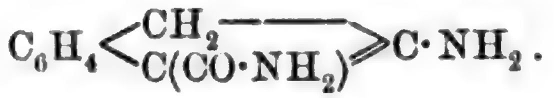
The *hydrochloride*, $C_{10}H_9O_2N,HCl$, can be prepared by cautiously dissolving the carboxylic acid in concentrated hydrochloric acid, filtering and allowing to stand, when slender, colourless needles of the salt separate. It is at once dissociated by water:

0·2318 gave 0·1564 AgCl. Cl = 16·69.

$C_{10}H_9O_2N,HCl$ requires Cl = 16·8 per cent.

2-Aminoindene-3-carboxylic acid gives a blue colour with concentrated sulphuric acid containing a trace of an oxidising agent.

2-*Aminoindene-3-carboxyamide*,



$$C_6H_4{<}\begin{matrix}CH_2\text{———}\\C(CO\cdot NH_2)\end{matrix}{>}C\cdot NH_2\,.$$

The portion of the product which remained undissolved after extracting 2-aminoindene-3-carboxylic acid in the above experiment with aqueous potash, was recrystallised from alcohol and obtained in pale yellow plates melting with decomposition at 202°:

0·2099 gave 0·5275 CO_2 and 0·1108 H_2O. C = 68·54; H = 5·86.

$C_{10}H_{10}ON_2$ requires C = 68·9; H = 5·7 per cent.

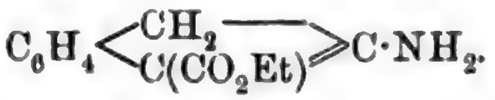
The amide forms salts with acids which are unstable in aqueous solution. The *hydrochloride*, $C_{10}H_{10}ON_2,HCl$, is prepared by dissolving the amide in concentrated hydrochloric acid and allowing the solution to stand. It forms colourless plates:

0·2158 gave 0·1462 AgCl. Cl = 16·76.

$C_{10}H_{10}ON_2,HCl$ requires Cl = 16·9 per cent.

When the amide is warmed with dilute aqueous potash, ammonia is evolved, and if, when the evolution is complete, the solution is acidified, 2-aminoindene-3-carboxylic acid separates from the solution.

Ethyl 2-aminoindene-3-carboxylate,



$C_6H_4{<}\begin{matrix}CH_2\text{———}\\C(CO_2Et)\end{matrix}{>}C{\cdot}NH_2$.

This substance can be prepared by the etherification, by alcohol and sulphuric acid, of the corresponding carboxylic acid. It was, however, conveniently prepared directly from β-imino-α-cyanohydrindene by the following process. Twenty grams of the imino-nitrile were dissolved in 200 c.c. of concentrated sulphuric acid in the manner already described, and after the solution had stood for one hour it was poured into three times its volume of absolute alcohol, and then heated on the water-bath for three hours. At the end of this time, the product was poured into water and the aqueous solution extracted with ether. The ethyl salt being very insoluble in ether remained for the most part suspended in the solvent, but the aqueous solution was clear and could be separated. The ethereal solution containing the ethyl salt in suspension was then shaken with dilute sodium carbonate solution to remove any unchanged acid, and then filtered. The solid thus obtained, on being recrystallised from alcohol, yielded flat, glistening, pale yellow needles melting at 206°:

0·3062 gave 0·7960 CO_2 and 0·1770 H_2O. C = 70·9; H = 6·4.

$C_{12}H_{13}O_2N$ requires C = 70·9; H = 6·4 per cent.

The ethyl salt is readily hydrolysed by dilute hydrochloric acid to 2-aminoindene-3-carboxylic acid.

The *hydrochloride*, $C_{12}H_{13}O_2N,HCl$.—The ethyl salt quickly dissolves in concentrated hydrochloric acid, and the solution on standing deposits the hydrochloride in colourless needles which are at once dissociated by water:

0·2297 gave 0·1363 AgCl. Cl = 14·68.

$C_{12}H_{13}O_2N,HCl$ requires Cl = 14·8 per cent.

Both the ethyl salt and the carboxylic acid give the characteristic blue colour with concentrated sulphuric acid containing a trace of an oxidising agent.

Elimination of Nitrogen from 2-Aminoindene-3-carboxylic Acid and from Ethyl 2-Aminoindene-3-carboxylate by means of Nitrous Acid.

2-Aminoindene-3-carboxylic Acid.—The experiment was carried out in such a manner that the nitrogen evolved by the action of nitrous acid could be measured. A weighed quantity of the acid was introduced into a small flask, in which it was brought into solution by means of a little sodium hydroxide. Excess of sodium nitrite solution was then added, and the flask connected on the one hand with a nitrometer filled with potassium hydroxide solution, and on the other with a carbon dioxide generating apparatus. At the same time, a dropping funnel was inserted in the neck of the flask. After all the air had been expelled by carbon dioxide, the solution in the flask was warmed to 80° and excess of hydrochloric acid run in slowly through the dropping funnel. When the evolution of nitrogen had ceased, the gas left in the flask was swept out by carbon dioxide and the amount of nitrogen measured:

0·2219 gave 23·5 c.c. of nitrogen at 18° and 756 mm.
$C_{10}H_9O_2N + HNO_2$ requires 23·8 c.c.

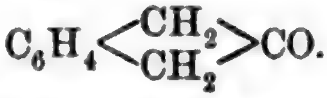
No trace of 2-hydroxyindene-3-carboxylic acid could be isolated from the products of this reaction, the chief compound formed being a yellow, amorphous substance which has not as yet been identified.

Ethyl 2-aminoindene-3-carboxylate.—The apparatus employed in this experiment was the same as that used above, only the weighed quantity of the ethyl salt, after being introduced into the flask, was dissolved in concentrated hydrochloric acid, and, after the air in the flask had been replaced by carbon dioxide, an excess of sodium nitrite solution was run in from the dropping funnel:

0·2138 gave 24·9 c.c. of nitrogen at 17° and 766 mm.
$C_{12}H_{13}O_2N + HNO_2$ requires 25·2 c.c.

In this case also no ethyl 2-hydroxyindene-3-carboxylate was formed in the reaction, the product consisting of an ill-defined resinous substance, evidently of high molecular weight.

β-Hydrindone,



$$C_6H_4<\substack{CH_2\\CH_2}>CO.$$

This substance was best produced from 2-aminoindene-3-carboxylic acid in the following way. Thirty grams of the acid were mixed with a solution of 80 grams of concentrated sulphuric acid in 240 of water, which was quickly raised to boiling and a rapid current of steam passed into it, when the hydrindone passed over as a colourless oil which solidified in the receiver. It was collected and recrystallised from alcohol, being obtained in large, colourless needles melting at 58°. These crystals showed no tendency to alter on exposure to the air.

The substance was further characterised by the formation of its phenylhydrazone, melting at 120°, and its oxime, melting at 152°. In preparing the phenylhydrazone, however, care must be taken not to boil the acetic acid solution of the reacting substances; otherwise a compound melting at 210° separates out which contains 6·8 per cent. of nitrogen. It is probably the phenylhydrazone of a condensation product. β-Hydrindone gives a deep blue colour with concentrated sulphuric acid containing a trace of an oxidising agent; an examination of the properties of this substance and of those of its derivatives is in progress.

Much of the expense entailed by this research has been met by a Grant from the Research Fund of the Chemical Society, for which we desire to express our indebtedness.

MANCHESTER UNIVERSITY.

XVIII.—*The Colour of Cupric Salts in Aqueous Solution.*

By NEVIL VINCENT SIDGWICK and HENRY THOMAS TIZARD.

THE question of the influence of electrolytic dissociation on colour has recently been the subject of much discussion. It is held by one school, following Ostwald, that dissociation alone is sufficient to account for a change of colour; whilst other chemists, such as Hantzsch, maintain that the colour of an undissociated molecule in solution is identical with that of the ions which it produces, and that the observed changes of colour are due to changes of constitution. It was with the view of obtaining some information on this question that the following experiments were carried out; and although the results are as yet inconclusive, they seem of sufficient interest to be worth recording.

The changes of colour shown by solutions of cupric salts have long been known, and have been the subject of many investigations. These have, however, been directed mainly to two points: either to showing that in very dilute solution the light-absorption of all cupric salts is the same, being that of the cupric ion, or to discovering the conditions which determine the fairly sharp change from blue to green or brown, exhibited by most cupric salts at high concentrations.

The first point may be taken as satisfactorily established for coloured ions in general, by the work of Ostwald (*Zeitsch. physikal. Chem.*, 1892, **9**, 579), Pflüger (*Ann. Physik*, 1903, [iv], **12**, 430), and others; the colour of an ion in a completely dissociated solution is unaffected by the other (colourless) ion by which it is accompanied. The second point is still somewhat obscure, but the researches of Donnan and Bassett (Trans., 1902, **81**, 939) make it probable that the change of tint in concentrated solution is due to the formation of complex ions or complex undissociated molecules.

Much less attention has been directed to the region lying between these two extremes, where the solution is sufficiently dilute to be blue, and yet is not wholly dissociated. Such work as has been done has all been spectroscopic, consisting either in the measurement of the absorption bands, or in the determination of the intensity of the absorption for light of certain definite wave-lengths. The former method is open to various objections; as Ewan says (*Phil. Mag.*, 1892, [v], **33**, 317): "It is quite possible that general absorption may exist in a spectrum which, not being sufficiently large altogether to extinguish the light at any place, may pass unnoticed." In the latter method (compare B. E. Moore, *Zeitsch. physikal. Chem.*, 1906, **55**, 641), the very abundance of data obtainable has so far prevented any definite quantitative relations being deduced, although various observers have noticed, for example, the great depth of colour of the acetate solution, and that this diminishes on dilution.

It seemed possible that a clearer view would be obtained by the direct quantitative determination of the depth of colour of the blue solutions of various cupric salts at varying dilutions. This we have endeavoured to carry out. The apparatus used was the Donnan tintometer (*Zeitsch. physikal. Chem.*, 1896, **19**, 465); the method of working is that of Donnan, slightly modified, as described by T. S. Moore and one of us (*Zeitsch. physikal. Chem.*, 1907, **58**, 385). The principle is simple. Two graduated glass tubes with plane glass bottoms are equally illuminated by an incandescent gas burner; one is filled with the liquid to be examined, the other with a standard solution the height of which can be altered at will. The upper surface of the liquid in both tubes is free. By a suitable arrangement of mirrors the lights transmitted by the two tubes are brought into immediate contiguity, and the level of the standard liquid adjusted until the two tints appear identical. The depth of colour of the liquid in the first tube is then directly proportional to the height of the standard liquid in the second. This apparatus will only compare two colours the tint of which is the same. Even a small difference in the nature of the colour makes it impossible to find a point of equality, and hence our measurements were necessarily limited by the concentration at which the green colour makes its appearance.

The standard used was an approximately fifth-(molecular)-normal copper sulphate solution, slightly acidified with sulphuric acid in order to eliminate any influence of alkali dissolved from the glass. It was not necessary to know the exact strength of this standard, as its value was determined each day by comparison with a solution of known strength and depth of colour. The experimental tubes were found by calibration to be of equal diameter throughout. Hence, if a known volume of a copper solution is placed in the tube, and successive quantities of water are added, the optical thickness (concentration of copper multiplied by thickness of layer) remains unaltered, the concentration itself being measured by the height of the liquid in the tube.

The simplest hypothesis is that the changes which accompany dilution, whether they consist in the breaking down of complexes, in ionic dissociation, or in changes in the state of hydration, do not involve any alteration in the absorption. If this is the case, the colour will be proportional to the optical thickness; moreover, the (colourless) anion, since it does not affect the colour at infinite dilution, will not affect it at any other dilution either. This, however, is not the case; the colour depends both on the concentration and on the nature of the anion. This dependence is most easily expressed by determining at various dilutions and for various salts what may be called the molecular depth of colour; that is to say, the amount of colour of a gram-molecule of the salt, dissolved in various quantities of water, and contained in a tube of uniform diameter, the colour of a gram-molecule of copper sulphate in 5 litres of water being taken as 1. This magnitude we denote by C_v.

The following example will make the method of calculation clear.

Each solution was measured by both of us separately, the mean of at least four concordant values for each observer being taken. If these means were not themselves concordant (within 0·5 mm. on a total height of from 4 to 12 cm.) the measurements were repeated. The temperature of observation was 18°.

Thus with cupric acetate the following values were obtained. Ten c.c. of a $N/5$ solution were taken and diluted to a height of 5·22 cm. (volume = 30 c.c. V, the volume of solution in litres containing 1 gram-molecule of the salt = 15). The readings of the standard were:

N. V. S.*	H. T. T.*
3·80 cm.	3·79 cm.
3·80 ,,	3·80 ,,
3·82 ,,	3·81 ,,
3·79 ,,	3·80 ,,
3·80 ,,	3·80 ,,

Mean, 3·80 cm.

Water was then added until the liquid stood at 6·09 cm. (Volume = 35 c.c. $V = 17·5$.) Readings:

N. V. S.	H. T. T.
3·75 cm.	3·70 cm.
3·71 ,,	3·72 ,,
3·71 ,,	3·70 ,,
3·72 ,,	3·70 ,,
3·72 ,,	3·70 ,,

Mean, 3·71 cm.

---

* Author's initials.

The tube was then filled with the $N/5$-copper sulphate solution to a height of 8·70 cm. (= 50 c.c.), and read again :

N. V. S.	H. T. T.
3·70 cm.	3·70 cm.
3·67 ,,	3·68 ,,
3·67 ,,	3·65 ,,
3·71 ,,	3·68 ,,
3·69 ,,	3·68 ,,

Mean, 3·69 cm.

Now, since 50 c.c. of the $N/5$ sulphate solution balance 3·69 cm. of the standard, 5,000 c.c. (containing 1 gram-molecule) in a tube of this diameter would balance 369 cm. This therefore is the unit of colour.

In the first case quoted, 30 c.c. of $N/15$ copper acetate balance 3·80 cm. Hence 15,000 c.c. (one gram-mol.) would balance $3·80 \times 500$ cm. Thus the value of C_v for the acetate at $V = 15$ is $\frac{3·80 \times 500}{369} = 5·15$. Similarly in the second case, where the optical thickness is the same, $C_v = \frac{3·72 \times 500}{369} = 5·02$.

The salts examined fall into two classes, which gave very different results : (1) those of weak acids (propionate, acetate, formate, monochloroacetate), and (2) those of strong acids (sulphate, chloride, bromide, and nitrate). The salts of the second class are very difficult to measure accurately. Their colour is very much paler than that of the weak acid salts, even in the strongest solutions, and the change of colour with dilution, which is always an increase, is very small ; but we give the results for what they are worth.

The weak acid salts, on the other hand, have a much deeper colour, which is deeper the weaker the acid, and the effect of dilution is much greater, and in the opposite direction, the colour diminishing with the concentration.

In the following tables, V represents the number of litres containing a gram-molecule, h the mean height of the balancing column of standard, and C_v the molecular depth of colour. The measurements of copper sulphate give the height of standard required to balance 8·70 cm. (50 c.c.) of the $N/5$ sulphate solution on each occasion. The temperature was in all cases 18°.

1. *Cupric Propionate.*—Three series of observations were made. The first two, (*a*) and (*b*), were not compared with the sulphate, but were referred through the values for $V = 20$ to (*c*), which was directly compared with the sulphate. In (*c*) the liquid was diluted up to a height of 15·66 cm. ($V = 22·5$) and then a portion was poured

away. The remainder, which measured 10·04 cm., was then further diluted, the necessary correction being applied in calculating C_v:

(*a*). 10 c.c. $N/5$ solution taken.

V.	h in cm.	C_v.
5	6·25	8·01
10	4·77	6·12
15	4·24	5·44
20	3·90	(5·00)

(*b*). 10 c.c. $N/5$ solution taken.

V.	h in cm.	C_v.
10	4·68	6·16
20	3·80	(5·00)
25	3·50	4·60
30	3·39	4·46
35	3·31	4·35
45	3·16	4·16

(*c*). 20 c.c. $N/5$ solution.

V.	h in cm.	C_v.
13	8·32	5·62
15	8·03	5·43
17·5	7·73	5·22
20	7·40	5·00
22·5	7·19	4·86
22·5	4·65	4·86
25	4·50	4·70
27·5	4·43	4·63
30	4·28	4·47
32·5	4·20	4·40

Copper sulphate : 50 c.c. $N/5$ solution.

V.	h in cm.	C_v.
5	3·70	1

2. *Cupric Acetate*: 10 c.c. $N/5$ solution.

V.	h in cm.	C_v.
5	4·86	6·59
7·5	4·39	5·95
10	4·13	5·59
12·5	3·99	5·41
15	3.80	5·15
17·5	3·71	5·03
20	3·61	4·89
25	3·49	4·73
30	3·38	4·58
40	3·22	4·36

Copper sulphate : 50 c.c. $N/5$ solution.

V.	h in cm.	C_v.
5	3·69	1

3. *Cupric Formate.*

(*a*). 10 c.c. $N/3$ solution.

V.	h in cm.	C_v.
3	4·84	3·90
9	4·03	3·25
12	3·89	3·14
15	3·88	3·13
18	3·83	3·09

Sulphate : 50 c.c. $N/5$ solution.

V.	h in cm.	C_v.
5	3·73	1

(*b*). 10 c.c. $N/3$ solution.

V.	h in cm.	C_v.
3	4·89	3·88
6	4·32	3·43
9	4·10	3·24

Sulphate : 50 c.c. $N/5$ solution.

V.	h in cm.	C_v.
5	3·78	1

4. *Cupric Monochloroacetate* : 10 c.c. normal solution.

V.	h in cm.	C_v.
1	13·97	3·74
2	11·82	3·17
3	10·92	2·92
4	10·38	2·78
5	10·08	2·70
6	9·85	2·64
7	9·44	2·53
8	9·30	2·50
9·6	8·89	2·38

Sulphate : 50 c.c. $N/5$ solution.

V.	h in cm.	C_v.
5	3·73	1

5. *Cupric Sulphate*: 10 c.c. normal solution.

V.	*h* in cm.	C_v.
1	3·44	0·91
2	3·62	0·95
3	3·75	0·98
4	3·72	0·98
5	3·80	1·00
6	3·83	1·01
7	3·94	1·04

6. *Cupric Chloride.*

(*a*). 10 c.c. normal solution.

V.	*h* in cm.	C_v.
3	3·45	0·96
4	3·58	0·98
5	3·63	1·01
6·5	3·64	1·01
7	3·61	1·00
Sulphate: 50 c.c. *N*/5 solution.		
5	3·61	1

(*b*). 10 c.c. normal solution.

V.	*h* in cm.	C_v.
2	3·69	0·95
4	3·82	0·98
6	3·83	0·98
9	3·98	1·02
Sulphate: 50 c.c. *N*/5 solution.		
5	3·90	1

7. *Cupric Bromide*: 20 c.c. 2*N*/3 solution.

V.	*h* in cm.	C_v.
3	4·60	0·94 (still green)
4·5	4·71	0·96
5	4·70	0·96
7	4·71	0·96
Sulphate: 50 c.c. *N*/5 solution.		
5	3·66	1

8. *Cupric Nitrate.*

(*a*). 10 c.c. normal solution.

V.	*h* in cm.	C_v.
1	3·91	1·08
2	3·84	1·06
3	3·89	1·07
4	3·90	1·07
5	3·91	1·08
7	3·97	1·10
9	4·06	1·12

(*b*). 10 c.c. 2*N* solution.

V.	*h* in cm.	C_v.
0·5	8·24	1·14
1	7·70	1·07
1·5	7·65	1·06
2	7·64	1·06
Sulphate: 50 c.c. *N*/5 solution.		
5	3·61	1

The curves given in Fig. 1 represent the relation between colour and concentration for the salts of weak acids. The curve for copper sulphate is added for comparison. It is not a straight line, but would appear practically straight on the scale employed.

In the case of the strong acids, the concentrations which could be investigated were limited on the one hand by that at which the solution assumes a green tint (or in the case of the sulphate by the solubility), and on the other by that at which the colour (even with a layer of 17 cm.) becomes too pale for measurement. This gives practically the limits of $V=1$ to $V=9$. The variations of colour within these limits are very small. They are represented in Fig. 2, the colour-scale being very large, but they cannot be regarded as having more than a qualitative value.

FIG. 1.

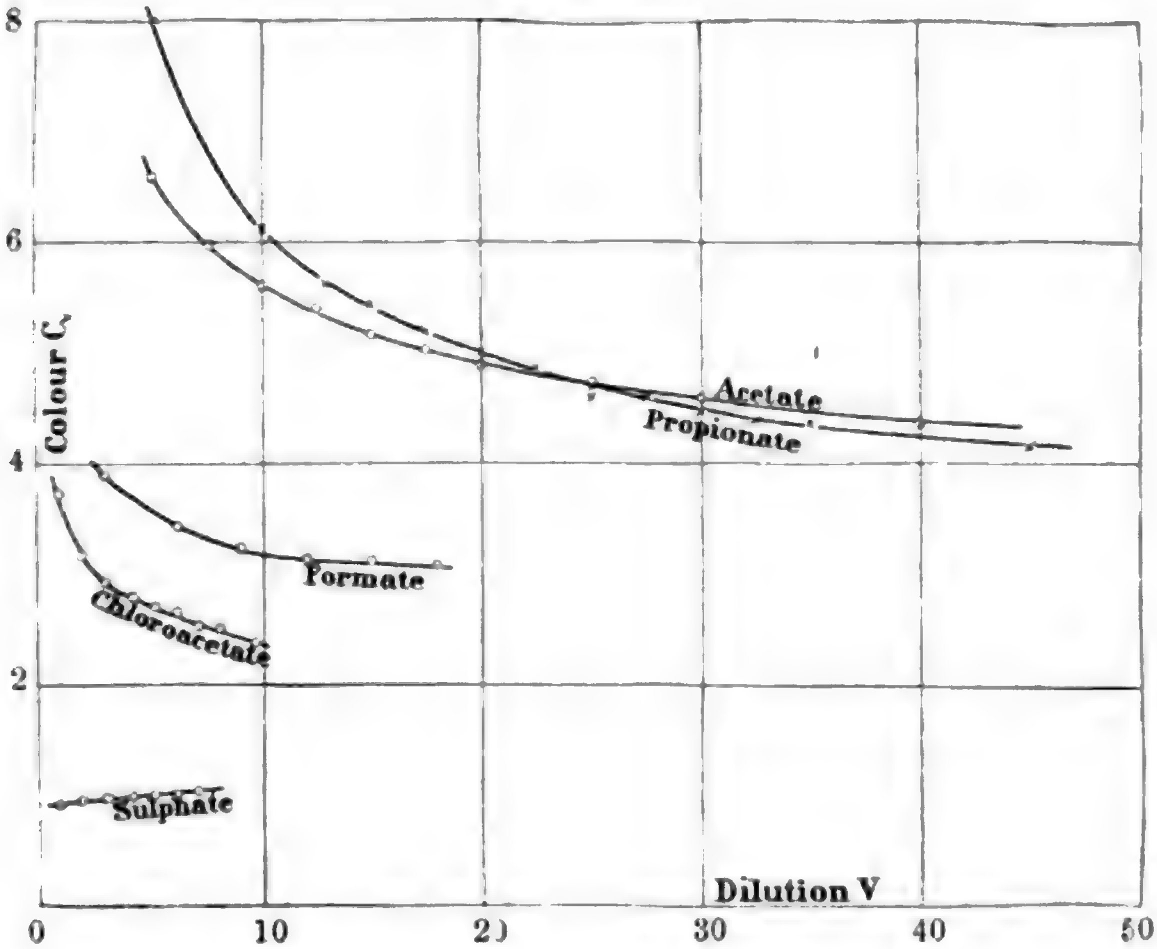
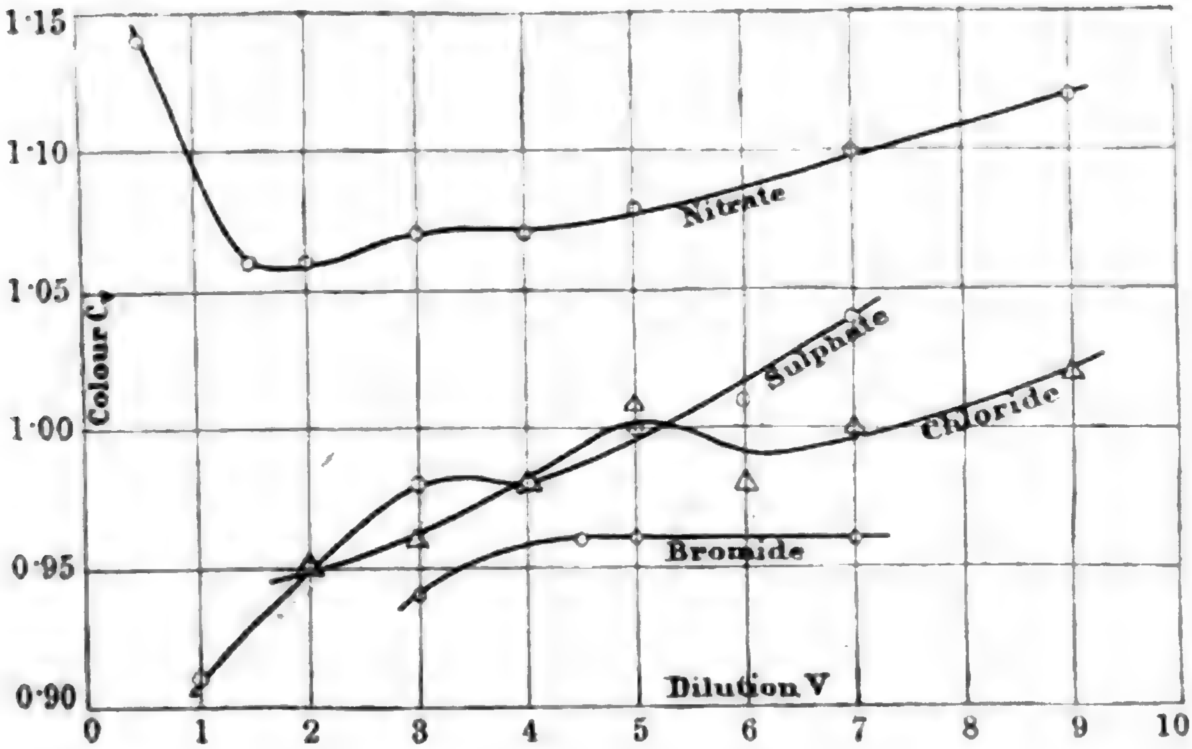


FIG. 2.



Discussion of Results.

1. *Weak Acid Salts.*—We may assume that at extreme dilution equivalent solutions of all cupric salts with colourless anions have the same tint and depth of colour. The value for infinite dilution cannot be determined by our method; but from the course of the curves for strong acid salts, where the change of colour with dilution is small, and the dissociation even at $V=9$ is already very large, it is probable that the limiting value of C_v is less than 1·5.

At the highest dilutions examined the salts of weak acids have a value of C_v considerably higher than this, rising from about two for the chloroacetate to four for the acetate and propionate. As the concentration increases, C_v increases also, and the more rapidly the weaker the acid,* until at about $V=4$, where it has reached for the acetate a value of 7, and for the propionate of more than 8, the solution begins to show a distinct greenish tinge, and further measurements become impossible.

It is therefore evident that these cupric solutions contain at least two substances of the same blue tint, but differing in depth of colour. The identity of tint is especially to be noticed, as it is not at all what we should expect. As it appears that the depth of colour of cupric solutions depends, except at extreme dilution, on the nature of the anion, it is clear that this is due at least to the recombination of the anion with the cupric cation, and hence the view that ionisation has no effect on colour is incorrect. But it would seem that, at least in these cases, it is only the depth of colour that is affected by the anion, and not the tint. As has been explained, all the solutions we examined, whether of strong or weak acids, were compared with the same standard, a $N/5$ copper sulphate solution; and up to a concentration of $N/4$ (in some instances much higher than this) no change of tint was observed, although the depth varied with the anion and the dilution in the proportion of 1 to 8. It follows that the cupric ion is capable of forming compounds in the solution of a different depth of colour, but of practically the same absorption in the visible part of the spectrum. These compounds may be of four kinds: either the univalent ions $CuA^{\cdot}$ (where A represents a univalent anion) and the undissociated molecules CuA_2, or complex ions such as CuA_4'', or the products of hydrolytic dissociation, or hydrates of any of these molecular species. The last of these possibilities may be left out of account, as practically nothing is known as to the constitution of these hydrates or their

---

* The dissociation constants of these acids are:—

Propionic, $K \times 10^4$	$=0·134$	Formic..........	$=$ 2·14
Acetic	0·180	Monochloroacetic ...	15·00

influence on colour (compare Donnan, *Zeitsch. physikal. Chem.*, 1905, **53**, 317). The recent work of Jones and Uhler (*Amer. Chem. J.*, 1907, **37**, 126, 207) is open to the general objections which apply to the spectrometric method, and, moreover, their plan of adding to the solution a colourless salt with the same anion must produce a disturbance of the ionic equilibrium the amount of which can scarcely be determined, and which they altogether fail to consider. The question of hydrolysis is one on which it is difficult to come to a definite conclusion, and there are no determinations of the amount of hydrolysis of salts of the type MX_2. But there are several reasons for thinking that its influence is small, and may be, at least provisionally, neglected. In the first place, if hydrolysis were the determining factor in the change of colour, we should expect this change to be much more rapid with the salts of the weakest acids (acetate and propionate) than with those of the much stronger formic and chloroacetic acids: whereas the reverse is the case. Again, it is not to be supposed that anything like complete hydrolysis has taken place at a dilution of *N*/40, at which the hydrolysis of sodium acetate is only 0·02 per cent., and even that of potassium cyanide is less than 3 per cent.; so that the colour-curves should still be tending downwards at this point, whereas they have become nearly horizontal. Finally, a rough idea of the influence of hydrolysis can be arrived at by observing the effect on the colour of adding free acetic acid to a copper acetate solution. The amount of hydrogen ions in the solution due to hydrolysis will be small compared with the total quantity of acetate ions, and hence the addition of free acid will greatly diminish the hydrolysis without much affecting the degree of ionic dissociation of the salt. Experiment showed that the colour of a solution of *N*/6 copper acetate was increased less than 1 per cent. by the presence of *N*/2 acetic acid. We therefore conclude that while hydrolysis must be regarded as a possible disturbing factor, it is not probable that it has an appreciable effect on our results.

As regards complex ions, it is probable, as Donnan has shown, that it is to the presence of complex anions containing copper that the green or brown colour of concentrated solutions is due.

We are therefore inclined to suggest that the point where the solution changes from green to blue is that at which these complex ions become negligible in quantity, and the solution contains no molecules other than CuA_2 and the ions $CuA^{\cdot}$, $Cu^{\cdot\cdot}$, and A'. Of these, the last, as we know, will have no influence on the absorption, and may be neglected. The absorption will therefore be due to the three species CuA_2, $CuA^{\cdot}$, and $Cu^{\cdot\cdot}$ (or some of them); identical in tint, but differing in depth of colour; and the change of colour on dilution will be caused by the production of the latter species at the expense of the former. On extreme dilution only $Cu^{\cdot\cdot}$ ions remain, whatever the nature of the anion, and here therefore all copper salts give the same absorption: the value of C_v for this, as we have shown, is probably between 1 and 1·5. If it were possible in any way to determine the amounts of CuA_2, $CuA^{\cdot}$, and $Cu^{\cdot\cdot}$ present in a solution, their colour-values could be calculated, and our hypothesis checked. But at present this does not appear to be possible. There is no means of measuring the amount of dissociation of a ternary salt, such as CuA_2. The conductivity is no guide, since we cannot determine the velocity of the ion $CuA^{\cdot}$, and the indirect methods which have been suggested, such as the measurement of the concentration of the ion A' by the solubility-product, are not sufficiently accurate.

If there are appreciable quantities of all the three coloured substances CuA_2, $CuA^{\cdot}$, and $Cu^{\cdot\cdot}$ present in the solution, both the changes $CuA_2 \longrightarrow CuA^{\cdot}$ and $CuA^{\cdot} \longrightarrow Cu^{\cdot\cdot}$ must occur on dilution. If the second of these occurs to an appreciable extent within the dilutions investigated, we should expect all the curves to tend to the same point, the colour of the $Cu^{\cdot\cdot}$ ion, $C_v = 1·5$. We should also expect a change in the nature of the curve at the point where the second dissociation began to make itself felt. But neither of these conditions is fulfilled. There is no change in the nature of the curves, and they each tend to a different limit, which is always greater than 1·5. From these results, and especially from the second, we infer that only one dissociation is taking place, and that this is the first one, $CuA_2 \longrightarrow CuA^{\cdot}$. This leads to a somewhat remarkable conclusion. It will be seen from the shape of the curves that whatever change has been going on during the dilution has very nearly reached its end at the highest dilutions observed, since at this point all the curves become very nearly horizontal. If, therefore, our view is correct, the second dissociation of a copper salt of a weak acid cannot begin to take place appreciably until the first has proceeded very far; whereas in the analogous case of the dibasic organic acids Ostwald has shown that the second dissociation takes place appreciably when the first is only half completed. In other words, in the copper salts of weak monobasic acids the second dissociation constant is very much smaller compared to the first than it is in the case of the organic dibasic acids themselves. And the reason for this is not far to seek. Ostwald has pointed out for the latter that in analogous series the larger the first ionisation-constant, the smaller the second. This he explains by the fact that the proximity of the two carboxyl groups, which increases the first ionisation-constant, at the same time diminishes the second, as the negative charge produced by the loss of the first hydrogen ion resists the appearance of a second negative charge, which must occur if a second hydrogen ion were split off; and does so to a greater extent the nearer it is to the second carboxyl. Now the extreme case of this effect would be where the two negative charges had to appear on the same atom; and here we should expect the strongest resistance to the second stage of the dissociation. But this is precisely what occurs with the salts of a bivalent metal such as copper and a monobasic acid.

If this view is correct, which seems at least possible, we have an explanation of the fact which appears very clearly from our curves, that the dissociation proceeds very far within the limits of dilution examined, and yet does not give any sign of the production of $Cu^{\cdot\cdot}$ ions, which would lead to a value of C_v below 1·5.

Now, if a is the molecular depth of colour of the molecule CuA_2, b that of the ion, $CuA^{\cdot}$, we have the relation,

$$C_v = a(1-x) + bx \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1),$$

where C_v is the colour at dilution V, and x is the degree of dissociation. Further, if we assume Ostwald's law, which recent research has shown to be probably justifiable even for strong electrolytes, we have

$$kV = \frac{x^2}{1-x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

By differentiating and eliminating x we arrive at the equation:

$$kV\left(-V\frac{dC_v}{dV}\right)\left(a - C_v + V\frac{dC_v}{dV}\right) = \left(a - C_v + 2V\frac{dC_v}{dV}\right)^2. \quad (3).$$

Now $\frac{dC_v}{dV}$ at any point may be obtained from the curve, so that we get a relation between a and k. By taking two points we can obtain values of a and k; their accuracy naturally depends on that of the curve and on that of the observation of $\frac{dC_v}{dV}$. From these values of a and k we can calculate b for every other point on the curve by means of equations (1) and (2).

The results we arrived at by applying this method to the weak acid curves confirm our hypothesis, as constant values of b are obtained in each case, while x, the degree of dissociation, rises to over 90 per cent. But as the numbers cannot, for the reasons we have given, be regarded as absolutely correct, but only relatively so, we propose to reserve their publication until we have obtained more trustworthy data.

(2). Strong acids. Here a regular curve was in no case obtained, but the curves all follow roughly the same course. The colour on the whole increases on dilution, but the change is very small. The case of the nitrate is of interest. At the point where the bromide and chloride become green, the colour of the nitrate (which is always blue) begins to increase rapidly. This indicates that in this case the complex ions have the same tint as the $Cu(NO_3)_2$ molecule, but are deeper in colour.

DAUBENY LABORATORY,
MAGDALEN COLLEGE,
OXFORD.

XIX.—*Organic Derivatives of Silicon. Part IV. The Sulphonation of Benzylethylpropylsilicyl Oxide and of Benzylethyldipropylsilicane.*

By HERBERT MARSDEN, B.Sc. (Vict.), and FREDERIC STANLEY KIPPING.

PHENYLBENZYLETHYLPROPYLSILICANE is hydrolysed by hot sulphuric acid giving benzene and benzylethylpropylsilicol (Kipping, Trans., 1907, **91**, 212); the latter undergoes sulphonation, yielding an acid which was regarded as the disulphonic derivative of benzylethylpropylsilicyl oxide and to which the constitution

$$SO_3H{\cdot}C_6H_4{\cdot}CH_2{\cdot}SiEtPr{\cdot}O{\cdot}SiEtPr{\cdot}CH_2{\cdot}C_6H_4{\cdot}SO_3H$$

was assigned. Subsequently (Kipping, Trans., 1907, **91**, 727) this same sulphonic acid was obtained by the sulphonation of benzylethylpropylsilicol, prepared directly by decomposing benzylethylpropylsilicyl chloride with water.

As this sulphonic acid is the only compound containing an asymmetric silicon group which, so far, has been resolved, and as the evidence that it was derived from the oxide and not from the silicol was, perhaps, not quite conclusive, we have made some further experiments in order to settle the matter.

For this purpose we examined the product of high boiling point which is formed together with benzylethylpropylsilicol when benzylethylpropylsilicyl chloride is decomposed with water, and found, as was indeed expected (*loc. cit.*, p. 726), that it consisted of the oxide $(BzEtPrSi)_2O$; this compound was then sulphonated with sulphuric acid and also with chlorosulphonic acid. In both cases the product was a mixture of acids, from which the isolation of a pure compound proved to be a task of some difficulty; ultimately, however, we obtained from both preparations an acid (in the form of its *l*-menthylamine salt) which was found to be identical with that previously described as sulphobenzylpropylsilicyl oxide.

Now as benzylethylpropylsilicyl oxide and other oxides of like nature are relatively very stable, whereas benzylethylpropylsilicol and other silicols are unstable and pass readily into the corresponding oxides, it seems extremely improbable that the oxide in question would be converted into the silicol during the process of sulphonation or subsequent treatment, and therefore the sulphonic acid may be regarded as derived from the oxide; as, moreover, this conclusion is fully borne out by the results of numerous analyses of the *l*-menthylamine salt which have been made in the course of these experiments, there is now not much room for doubt that the optically active silicon compounds recently described (*loc. cit.*, p. 234) are derivatives of benzylethylpropylsilicyl oxide.

The resolution of the sulphonic derivative of benzylmethylethylpropylsilicane, BzMeEtPrSi, and of other compounds containing only one asymmetric silicon group having so far been unsuccessful, we studied the sulphonation of phenylbenzylethylpropylsilicane,

PhBzEtPrSi,

with chlorosulphonic acid, in the hope that this agent would not have the hydrolysing action of sulphuric acid; unfortunately, however, we were unable to prepare the simple sulphonic derivative of this silicohydrocarbon, since the phenyl group was eliminated previous to, or during, sulphonation, and the same acid was obtained as by the use of sulphuric acid. The great difference in the behaviour of the phenyl and benzyl groups when combined with silicon is again shown by these results, and it may be noted that in these, as in other experiments, the phenyl radicle alone seems to be easily displaced.

This paper also contains an account of the investigation and utilisation of certain by-products which had accumulated in the preparation of silicon derivatives. Thus from a mixture of benzylethylsilicon dichloride and benzylethylpropylsilicyl chloride, obtained in the preparation of the latter, we prepared *benzylethyldipropylsilicane*, $BzEtPr_2Si$, and sulphonated this silico-hydrocarbon in order to compare the acid with the *dl*-derivative of benzylmethylethylpropylsilicane (*loc. cit.*, p. 731). Although one of these sulphonic derivatives is externally compensated, whereas the other is not, there is very great similarity in properties even when they are combined with an asymmetric base; the l-*menthylamine* salt of *benzylethyldipropylsilicanesulphonic acid*, for example, is indistinguishable by inspection from the corresponding salt of *dl*-benzylmethylethylpropylsilicanesulphonic acid and the resemblance in all ordinary properties is very striking; the *cinchonidine* and *quinine* salts of the two acids are also very similar, and the results of the comparison point strongly to the conclusion that these derivatives of the *dl*-acid are mere mixtures and not definite partially racemic salts.

Diphenylethylsilicyl chloride, $Ph_2EtSiCl$, was isolated from a by-product obtained in the preparation of phenylethylsilicon dichloride (*loc. cit.*, p. 215), but the corresponding silicol could not be obtained in a pure state owing to the readiness with which it passes into *diphenylethylsilicyl oxide*, $(Ph_2EtSi)_2O$, a crystalline compound melting at 65·5°.

Triphenylethylsilicane, Ph_3EtSi, and *triphenylmethylsilicane*, Ph_3MeSi, were also prepared from triphenylsilicyl chloride.

Benzylethylpropylsilicyl Oxide, $(BzEtPrSi)_2O$.

When benzylethylpropylsilicyl chloride is decomposed with water it yields a mixture of benzylethylpropylsilicol (Trans., 1907, **91**, 726) and benzylethylpropylsilicyl oxide; the two compounds are easily separated by fractional distillation under reduced pressure (25 mm.), the silicol boiling at about 155°, the oxide at about 256°. A sample of the oxide boiling at 271—272° (50 mm.) was analysed:

0·2403 gave 0·6313 CO_2 and 0·2079 H_2O. $C = 71·6$; $H = 9·6$.

$C_{24}H_{38}OSi_2$ requires $C = 72·2$; $H = 9·5$ per cent.

Benzylethylpropylsilicyl oxide is a rather viscid, colourless, almost odourless liquid, insoluble in water, but miscible with the ordinary organic solvents.

Sulphonation of Benzylethylpropylsilicyl Oxide with Sulphuric Acid.

When benzylethylpropylsilicyl oxide in quantities of about 10 grams at a time is treated with 1½—2 volumes of sulphuric acid only a slight rise in temperature occurs; on heating quickly and shaking vigorously a very viscous, homogeneous fluid results, and by the time the temperature has risen to 70° or 80° sulphonation is complete, as shown by the solubility of the product in a moderately large quantity of water. The rapidity with which sulphonation occurs seems to be rather greater than in the case of the corresponding silicol, as was perhaps to be expected.

In the hope of isolating a crystalline ammonium salt, the aqueous solution of the acid was neutralised with ammonia, the ammonium sulphate separated by the method previously described (*loc. cit.*, p. 225), and the dried syrupy ammonium salt of the sulphonic acid dissolved in methyl alcohol; on adding a large volume of ethyl acetate to this solution, practically the whole of the dissolved salt was precipitated as a buttery mass, and the mother liquor did not contain any appreciable quantity of dissolved matter; this behaviour is very different from that of the crude ammonium salt obtained from the sulphonation product of benzylethylpropylsilicol; moreover, fractional precipitation of the buttery ammonium salt with ethyl acetate, from its solution in methyl alcohol, failed to alter its character appreciably, so that no crystallised ammonium sulphobenzylethylpropylsilicyl oxide could be isolated. This result seemed to show that the sulphonation products of the silicol and of the oxide were entirely different, but as a matter of fact they both contain sulphobenzylethylpropylsilicyl oxide, and the great difference in behaviour of the crude ammonium salts must be attributed to the accompanying by-products; why the latter should be so different it is difficult to conjecture. This method of purification having failed, the crude ammonium salt was treated in aqueous solution with *l*-menthylamine hydrochloride, and the oily precipitate of menthylamine salt separated; this was fractionally crystallised from ice-cold aqueous acetone, from which a considerable proportion was deposited in a flocculent condition, the remainder as an oil. After many recrystallisations, employing aqueous acetone, aqueous methyl alcohol, or wet ethyl acetate, some of the menthylamine salt was obtained in opaque nodules melting, when previously dehydrated, at about 215—220°; the further purification of this product proved to be very troublesome, but when systematically recrystallised, using aqueous acetone and wet ethyl acetate alternately for each series of operations, it finally yielded a well-defined, crystalline menthylamine salt melting at about 230°.

The details of these operations are omitted, but it may be noted that the great difficulty met with in isolating this salt is doubtless due to the presence of an isomeride which has not only a most baneful effect in preventing crystallisation, but which also remains very tenaciously in the crystalline deposits; when a considerable proportion of this isomeride is present, the mixture of salts is readily soluble in cold, wet ethyl acetate, whereas the pure compound melting at about 230° is practically insoluble.

The *menthylamine* salt (m. p. 230°) obtained in this way from the oxide resembled *l*-menthylamine sulphobenzylethylpropylsilicyl oxide (*loc. cit.* pp. 229, 729) in appearance, and like the latter crystallised with four molecules of water; a mixture of the two salts melted at the same temperature as its components:

0·2105 dried in the air lost 0·0165 H_2O at 100°. $H_2O = 7·8$.
$C_{44}H_{80}O_7N_2S_2Si_2 + 4H_2O$ requires $H_2O = 7·65$ per cent.
0·1662 gave 0·3682 CO_2 and 0·1377 H_2O. $C = 60·4$; $H = 9·2$.
0·1925 ,, 0·4267 CO_2 ,, 0·1598 H_2O. $C = 60·4$; $H = 9·2$.
$C_{44}H_{80}O_7N_2S_2Si_2$ requires $C = 60·8$; $H = 9·2$.

The equivalent of the salt was also determined, the value obtained being 437·2 instead of 434·4 required by theory.

The specific rotation was observed in methyl-alcoholic solution ; 0·3558, made up to 25 c.c. in a 2-dcm. tube, gave $\alpha -0{\cdot}49^\circ$, whence $[\alpha]_D\ -17{\cdot}1^\circ$.

All these results agree with those required for the menthylamine salt of a disulphonic acid derived from the oxide $(SiEtPrBz)_2O$, and if the identity of this salt with that previously described is established, little doubt will remain as to the constitution of the latter.

Now in one respect the menthylamine salt isolated from the sulphonation product of the oxide appeared to differ from that obtained directly from pure ammonium sulphobenzylethylpropylsilicyl oxide ; it did not seem to crystallise quite so readily or to form such large crystals.* For this reason some of the *l*-menthylamine salt prepared from the oxide was converted into sodium salt, and from the latter the cinchonidine and *d*-bornylamine salts were prepared ; the cinchonidine salt melted at 148—150° and its specific rotation in methyl alcohol was $[\alpha]_D\ -71{\cdot}1^\circ$, values agreeing closely with those of the cinchonidine sulphobenzylethylpropylsilicyl oxide previously prepared from the silicol (*loc. cit.*, p. 232) ; the properties of the bornylamine salt also agreed with those of the corresponding bornylamine salt from the silicol. There can be no doubt therefore that the silicol and the oxide yield one and the same acid when sulphonated under similar conditions, and that the sulphonic acid which has been resolved is in fact a derivative of the oxide. The by-products or other acids formed during these sulphonations have not yet been isolated.

Sulphonation of Benzylethylpropylsilicyl Oxide with Chlorosulphonic Acid.

The use of chlorosulphonic acid for the sulphonation of benzylmethylethylpropylsilicane gave results so much better than those obtained with sulphuric acid that it seemed advisable to try the action of the first-named agent on benzylethylpropylsilicyl oxide.

Chlorosulphonic acid (2 mols.) diluted with chloroform was added to a well-cooled solution of the oxide (1 mol.) in about five volumes of chloroform ; sulphonation occurred rapidly, with evolution of hydrogen chloride, and the solution was then immediately poured into water, and the chloroform distilled in steam ; the clear aqueous solution of the acid was neutralised with ammonia, treated with excess of *l*-menthylamine hydrochloride, and the oily menthylamine salt separated and washed; it soon solidified, and was then fractionally crystallised from aqueous acetone. The several deposits were further treated systematically with moist ethyl acetate and acetone, alternately, and finally a menthylamine salt, melting at about 230°, was isolated.

---

* This difference between the two salts is possibly caused by some slight difference in the relative quantities of their components. The salt prepared directly from the ammonium salt contains equal quantities of *dAlB* and *lAlB*, whilst that finally obtained from the oxide may contain unequal quantities of these components, partial resolution having occurred as a result of repeated fractional crystallisation.

This preparation was proved to be identical with the compound obtained by sulphonating the oxide with sulphuric acid; the dehydrated salt was analysed:

0·2044 gave 0·4532 CO_2 and 0·1705 H_2O. C = 60·5; H = 9·3.
0·1661 „ 0·3675 CO_2 „ 0·1409 H_2O. C = 60·3; H = 9·4.
0·2133 „ 0·4742 CO_2 „ 0·1848 H_2O. C = 60·6; H = 9·6.
$C_{44}H_{80}O_7N_2S_2Si_2$ requires C = 60·8; H = 9·2 per cent.

The isolation of a pure menthylamine salt from the product just described seemed to offer less difficulty than when sulphuric acid was used as the sulphonating agent, but as the two series of experiments were carried out at rather distant intervals, the behaviour of the two crude preparations was not directly compared.

Sulphonation of Phenylbenzylethylpropylsilicane with Chlorosulphonic Acid.

Since phenylbenzylethylpropylsilicane is hydrolysed by sulphuric acid with separation of benzene (*loc. cit.*, p. 223), some experiments were made to see whether hydrolysis could be avoided, and a monosulphonic derivative of the silico-hydrocarbon obtained by using chlorosulphonic acid.

Pure phenylbenzylethylpropylsilicane was dissolved in chloroform, and chlorosulphonic acid (1 mol.), also dissolved in chloroform, was slowly added, cooling in ice: towards the end of the operation hydrogen chloride was evolved, but on testing a small quantity of the solution it was found to contain a large proportion of an oil which was insoluble in water. A chloroform solution of chlorosulphonic acid (1 mol.) was then slowly run in, testing from time to time, but it was not until the whole of this had been added that the sulphonation was complete. These observations seemed to show that the silico-hydrocarbon was first decomposed by the chlorosulphonic acid, probably in accordance with the following equation: $SiPhBzEtPr + SO_3HCl = SiBzEtPrCl + C_6H_5{\cdot}SO_3H$.

The chloroform having been distilled in steam, the clear aqueous solution was neutralised with ammonia, and treated with excess of *l*-menthylamine hydrochloride: the precipitated menthylamine salt soon solidified and was repeatedly crystallised, using first aqueous acetone, then anhydrous acetone, and finally wet ethyl acetate; from the last-named solvent the salt was ultimately obtained in colourless, lustrous, hydrated crystals melting at about 230°.

The anhydrous salt was analysed:

0·1888 substance gave 0·4192 CO_2 and 0·1573 H_2O. C = 60·5; H = 9·3.
0·1628 „ „ 0·3625 CO_2 „ 0·1376 H_2O. C = 60·7; H = 9·4.

These results agree with those (C = 60·8; H = 9·2) required for the menthylamine salt derived from benzylethylpropylsilicyl oxide, and the identity of this preparation with the latter was completely established. The action of chlorosulphonic acid on the silico-hydrocarbon, therefore, is similar to that of sulphuric acid as regards the elimination of the phenyl radicle.

Benzylethyldipropylsilicane.

In the preparation of benzylethylpropylsilicyl chloride from molecular proportions of benzylethylsilicon dichloride and magnesium propyl bromide, a considerable proportion of the dichloride seems to be unchanged (*loc. cit.*, p. 722); after fractionally distilling the product many times, and separating the benzylethylpropylsilicyl chloride and compounds of higher boiling point, there remains a liquid which passes over from about 180—190°, and which is doubtless a mixture of the dichloride and its propyl derivative.

This material was utilised for the preparation of benzylethyldipropylsilicane, and for this purpose it was treated with excess of magnesium propyl bromide in the usual way; in order to ensure complete interaction the ether was then distilled and the pasty mass heated in an oil-bath at 130° for about two hours. After cooling and dissolving the magnesium salts in water, the oily product was separated and submitted to systematic fractional distillation. The liquid finally collected at 178° (50 mm.) was redistilled under atmospheric pressure and the portion boiling at 280° was analysed:

0·1708 gave 0·4710 CO_2 and 0·1729 H_2O. C = 75·2; H = 11·2.

$C_{15}H_{26}Si$ requires C = 76·8; H = 11·1 per cent.

Benzylethyldipropylsilicane is a colourless, mobile, highly refractive liquid, very similar to benzylmethylethylpropylsilicane and other homologues which have already been described.

Sulphonation of Benzylethyldipropylsilicane with Chlorosulphonic Acid.

The sulphonic derivative of benzylethyldipropylsilicane was obtained very easily by treating the silico-hydrocarbon with chlorosulphonic acid; the operation was carried out in chloroform solution, and the acid then converted into its ammonium salt exactly as described in the preparation of ammonium benzylmethylethylpropylsilicanesulphonate (*loc. cit.*, p. 739.) The ammonium salt was next treated with *l*-menthylamine hydrochloride in aqueous solution, and the colourless, solid precipitate separated by filtration.

l-*Menthylamine Benzylethyldipropylsilicanesulphonate*,
$SiEtPr_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}SO_3H,C_{10}H_{19}{\cdot}NH_2$.

The crude salt is readily soluble in wet light petroleum, but separates on cooling in lustrous, rather poorly defined plates; after repeated crystallisation from this solvent it is obtained in a pure condition, a small quantity of some oily by-product passing into the mother liquors.

A sample of the salt dried in the air until constant was heated at 100°:

0·2240 lost 0·0159 H_2O. $H_2O = 7{\cdot}1$.

$C_{25}H_{47}O_3NSSi + 2H_2O$ requires $H_2O = 7{\cdot}1$ per cent.

An analysis of the anhydrous salt gave the following result:

0·1143 gave 0·2667 CO_2; 0·1050 H_2O. $C = 63{\cdot}6$; $H = 10{\cdot}2$.

$C_{25}H_{47}O_3NSSi$ requires $C = 63{\cdot}9$; $H = 10{\cdot}0$ per cent.

The equivalent of the salt was also determined by the method previously used; the value obtained was 470·8 instead of 469·4 required by theory.

The specific rotation was determined in methyl-alcoholic solution:

0·589, made up to 25 c.c. in a 2-dcm. tube, gave α $-0{\cdot}70°$, whence $[\alpha]_D - 14{\cdot}9°$.

Anhydrous *menthylamine benzylethyldipropylsilicanesulphonate* melts at 135°, the hydrated compound at 62·5—63°; it is practically insoluble in water, but very readily soluble in all the ordinary organic solvents, including dry light petroleum; a concentrated solution of the salt in this solvent does not yield crystals when kept over sulphuric acid, but on adding a little water, the hydrated compound separates almost immediately on the water globules, and when the petroleum is thoroughly wetted almost the whole of the salt is quickly deposited.

In this respect, in outward properties, and in general behaviour this salt closely resembles the corresponding derivative of *dl*-benzylmethylethylpropylsilicanesulphonic acid (*loc. cit.*, p. 735), so closely, in fact, that the latter can hardly be regarded as a definite partially racemic compound. The specific rotation of the salt of the dipropyl derivative is also very nearly the same as that of the derivative of the externally compensated acid, which was found to be $[\alpha]_D$ $-15°$ in methyl-alcoholic solution.

Cinchonidine Benzylethyldipropylsilicanesulphonate.

The pure menthylamine salt was decomposed with the theoretical quantity of sodium carbonate, the menthylamine distilled in steam, and the resulting sodium salt treated with cinchonidine hydrochloride, ($C_{19}H_{22}ON_2,HCl + 2H_2O$), in aqueous solution; the precipitated *cinchonidine salt* was then recrystallised several times from aqueous alcohol, from which it separated in lustrous prisms melting at 191—192°. The salt is readily soluble in most of the ordinary organic solvents, but only sparingly so in cold ethyl acetate or ether, and practically insoluble in light petroleum or water.

Its specific rotation was determined in methyl-alcoholic solution:

0·4797, made up to 25 c.c. in a 2-dcm. tube, gave α $-2·66°$, whence $[\alpha]_D$ $-69·3°$.

The resemblance between this salt and the corresponding derivative of the *dl*-acid (*loc. cit.*, p. 743) is extremely close, the latter melting at 194—195°, and having a specific rotation $[\alpha]_D$ $-72°$.

Cinchonidine Hydrogen Benzylethyldipropylsilicanesulphonate.

This salt was obtained by treating the normal salt with excess of hydrochloric acid in methyl-alcoholic solution and then precipitating with water; the oily product soon solidified, and was then recrystallised from aqueous acetone. It crystallises in needles, melting and decomposing at 222—224°, and resembles the corresponding salt of the *dl*-acid in its behaviour towards solvents.

Quinine Benzylethyldipropylsilicanesulphonate.

The addition of a solution of quinine hydrochloride to a solution of the sodium salt caused the precipitation of an oil which soon solidified. The precipitate was washed well with water and crystallised from a mixture of ethyl acetate and light petroleum until a constant melting point was attained.

The salt formed long, colourless, lustrous needles, melted sharply at 175°, and was readily soluble in ethyl acetate, alcohol, acetone, ether, or benzene, but practically insoluble in light petroleum or water.

Its specific rotation was determined in methyl-alcoholic solution:

0·216, made up to 25 c.c. in a 2-dcm. tube, gave α $-1·94°$, whence $[\alpha]_D$ $-112·3°$.

Quinine Hydrogen Benzylethyldipropylsilicanesulphonate.

This compound was obtained from the normal salt in the usual manner and crystallised from aqueous methyl alcohol, from which it separated in long, colourless needles melting at 223—224°. It was soluble in chloroform, but practically insoluble in ethyl acetate, anhydrous acetone, or ether. This, and the normal quinine salt, were very similar to the corresponding derivatives of the *dl*-acid (*loc. cit.*, p. 742).

Diphenylethylsilicyl Chloride, $SiPh_2EtCl$.

The interaction of ethylsilicon trichloride and magnesium phenyl bromide has already been described (*loc. cit.*, p. 215), and it has been stated that after isolating the main product, phenylethylsilicon dichloride, by fractional distillation there remains a considerable quantity of a dark yellow or brown oil boiling above 240° (atmospheric pressure). This by-product, accumulated from many preparations, was submitted to systematic fractional distillation under reduced pressure, using a rod and disk column, and ultimately, after separating the diphenyl, three silicon compounds were isolated from it, namely, diphenylethylsilicyl chloride, triphenylsilicyl chloride, and triphenylsilicol.

Diphenylethylsilicyl chloride is a fuming, mobile liquid, boiling at about 240° (115 mm.) and at 206—208° (50 mm.); the freshly-distilled liquid was colourless, but after a short time some of the fractions became pink, some green, probably owing to traces of impurity. The fraction collected at 206—208° (50 mm.), after many distillations under different pressures, did not alter in boiling point appreciably when re-distilled, and on analysis:

0·9329 gave 0·5524 AgCl. Cl = 14·6.

A volumetric estimation of the chlorine in the same sample gave: Cl = 14·1.

$C_{14}H_{15}ClSi$ requires Cl = 14·4 per cent.

Diphenylethylsilicyl chloride reacts readily with *p*-toluidine in light petroleum solution, but the product could not be separated from the *p*-toluidine hydrochloride without adding water, the result being that the toluidide was completely decomposed.

Diphenylethylsilicyl Oxide, $(Ph_2EtSi)_2O$.

Diphenylethylsilicol, like benzylethylpropylsilicol (*loc. cit.*, p. 726) and phenylethylpropylsilicol (*loc. cit.*, p. 219), shows a great tendency to pass into the corresponding oxide, and up to the present no preparation giving satisfactory analytical results has been obtained. When diphenylethylsilicyl chloride is decomposed with water, the resulting oil extracted, and kept over sulphuric acid, a crystalline substance is deposited in the course of a few days. This product is the oxide; it separates from aqueous methyl alcohol in well-defined, colourless, rhomboidal plates melting at 65—66°, and is readily soluble in the common alcohols, but only moderately so in cold chloroform, ether, light petroleum, or benzene:

0·1487 gave 0·4141 CO_2 and 0·0927 HO_2. C = 76·0; H = 6·9.
0·1591 „ 0·4446 CO_2 „ 0·0980 H_2O. C = 76·2; H = 6·8.
$C_{28}H_{30}OSi_2$ requires C = 76·6; H = 6·8 per cent.

The conditions under which the silicol passes into the oxide and vice versa have not yet been studied.

Triphenylsilicyl Chloride, Ph_3SiCl.

The fractions of the crude by-product (p. 207) collected from about 260—330° (50 mm.) solidified more or less completely, and the crystalline deposit was separated by filtration and then washed with light petroleum in a stream of dry air. After several crystallisations from boiling light petroleum, in which the substance was readily soluble, it was obtained in colourless prisms melting at 110—111°. This product did not fume appreciably in the air, but as it was readily decomposed by water, it was necessary to exclude all moisture during its purification; it gave an immediate precipitate of silver chloride when added to an alcoholic solution of silver nitrate, and on exposure to the air it underwent decomposition, giving, after many days' exposure, a sample of triphenylsilicol melting at about 145—147°.

The following analysis of the compound and its behaviour towards water showed that it was triphenylsilicyl chloride:

0·2507 gave (volumetrically) 0·0303 Cl. Cl = 12·1.
$C_{18}H_{15}ClSi$ requires Cl = 12·0 per cent.

The occurrence of this compound in the product of the interaction of ethylsilicon trichloride and magnesium phenyl bromide is possibly due to the presence of silicon tetrachloride as impurity in the ethyl derivative used, but as the latter had been carefully fractionated, and as the relative quantity of the triphenyl derivative was considerable, it may be that the ethyl is displaced by the phenyl group during the interaction.

It may be noted that triphenylsilicyl chloride was first obtained in small quantities by Kipping and Lloyd (Trans., 1901, **79**, 449), but the melting point given by them is far too low; unless there is plenty of material at disposal for recrystallisation, it is difficult to avoid some slight decomposition by atmospheric moisture, and the melting point then rapidly falls.

Triphenylsilicol, Ph_3SiOH.

The fractions of the by-product (p. 207) collected from about 330—380° (50 mm.) also solidified partly, owing to the deposition of a compound free from halogen; this was separated and recrystallised from a mixture of ether and light petroleum, from which it was obtained in lustrous prisms melting at 150·5—151·5° (uncorrected):

0·2099 gave 0·6042 CO_2 and 0·1142 H_2O. C = 78·5; H = 6·0.

$C_{18}H_{16}OSi$ requires C = 78·2; H = 5·8 per cent.

This compound was identified as triphenylsilicol, the presence of which might naturally be ascribed to the unavoidable action of atmospheric moisture on the corresponding chloride during distillation, &c., but as it was obtained in such large relative quantities its occurrence may possibly be due to the decomposition of the ether used in the Grignard reaction.

The melting point of triphenylsilicol has been variously given as 139—141° (Polis, *Ber.*, 1886, **19**, 1019), 148° (Kipping and Lloyd, *loc. cit.*), 155° (Dilthey and Eduardoff, *Ber.*, 1904, **37**, 1139), 148—150° (Ladenburg, *Ber.*, 1907, **40**, 2274); a sample of the silicol prepared from the chloride was repeatedly crystallised from a mixture of ether and light petroleum until three successive fractions melted simultaneously; this preparation had the melting point given above (150·5—151·5°).

Triphenylethylsilicane, $SiPh_3Et$.

This silico-hydrocarbon was prepared by treating triphenylsilicyl chloride with excess of magnesium ethyl bromide; as no rise in temperature occurred on mixing the reagents, the ether was distilled off, and the residue heated in an oil-bath at 130° for three hours. After cooling and adding water, the product, which separated as a colourless solid, was crystallised several times from light petroleum. The yield was practically theoretical:

0·1771 gave 0·5390 CO_2 and 0·1113 H_2O. C = 83·0; H = 7·0.

$C_{20}H_{20}Si$ requires C = 83·2; H = 6·9 per cent.

Triphenylethylsilicane crystallises in rhomboidal prisms melting at 76°, and is readily soluble in light petroleum, ether, chloroform, benzene, ethyl acetate, or acetone, only moderately so in alcohol, and insoluble in water.

This silico-hydrocarbon seems to have been obtained recently by

Ladenburg* (*Ber.*, 1907, **40**, 2274), together with triphenylsilicane, by heating triphenylsilicyl bromide with zinc ethyl; according to Ladenburg, the melting point is 72—74°.

Triphenylmethylsilicane, $SiPh_3Me$.

This compound was prepared from triphenylsilicyl chloride and magnesium methyl iodide in a similar manner, heating at 130° for three hours. It was purified by recrystallisation from light petroleum, a theoretical yield being obtained:

0·1773 gave 0·5389 CO_2 and 0·1053 H_2O. C = 82·9; H = 6·6.

$C_{19}H_{18}Si$ requires C = 83·1; H = 6·6 per cent.

This compound melts at 67—67·5°, but otherwise it resembles the ethyl derivative very closely.

Government grants, for which the authors are greatly indebted to the Committee of the Royal Society, have been used to cover a portion of the cost of this investigation.

UNIVERSITY COLLEGE,
NOTTINGHAM.

XX.—*The Esterification Constants of the Normal Fatty Acids.*

By JOHN JOSEPH SUDBOROUGH and JAMES MYLAM GITTINS.

In previous papers (Trans., 1899, **75**, 467; 1904, **85**, 534; 1905, **87**, 1840; 1907, **91**, 1033), the esterification constants of the acids belonging to different series have been tabulated, and important conclusions drawn between constitution and rate of esterification, but so far quantitative measurements of the velocities of esterification of the normal fatty acids have not been made. We have made a series of determinations for the commoner normal acids, and the results are recorded in the present paper. We wished to determine these constants, not merely for their own sake, but also because we desired to compare these values with those obtained for the phenylated acids of formulæ $C_6H_5{\cdot}CO_2H$, $C_6H_5{\cdot}CH_2{\cdot}CO_2H$, $C_6H_5{\cdot}[CH_2]_2{\cdot}CO_2H$, $C_6H_5{\cdot}[CH_2]_3{\cdot}CO_2H$, and $C_6H_5\cdot[CH_2]_4\cdot CO_2H$. We also wished to compare the values obtained for certain unsaturated acids with those of their saturated analogues, and finally we desired to make a comparison between the fatty acids and some of the simpler ketonic acids in order to determine the effect of the replacement of two atoms of hydrogen by one of oxygen on the rate of esterification. The values obtained for the phenylated and ketonic acids we hope to present shortly to the Society.

---

* According to Ladenburg (*loc. cit.*), triphenylsilicol dissolves in fuming sulphuric acid on warming gently, and is converted into its trisulphonic acid. This statement was so difficult to reconcile with the results obtained by Kipping and Lloyd (*loc. cit.*), and also with more recent experience on silicon compounds, that a communication was made to Prof. Ladenburg on the subject, and in consequence he has expressed his intention of dealing with the matter in the *Berichte*.—F. S. K.

The methyl alcohol used in the experiments described in this paper was Kahlbaum's No. 1, free from acetone, and was purified by being boiled with 1·5 per cent. of metallic calcium in the form of turnings and subsequent distillation (compare Klason and Norlin, *Arkiv. Kem. Min. Geol.*, 1906, **2**, No. 24). The reaction between the alcohol and metal is much more vigorous when the metal has been freshly turned; bought turnings have but little action. The specific gravity of the purified alcohol was $D^{15\cdot5}_{4}$ 0·7952, and it was found to give values for cinnamic acid within 2 per cent. of those obtained by samples of methyl alcohol previously used, so that these results are comparable with those obtained for other acids with the exception of a few unsaturated acids (Trans., 1907, **91**, 1033). The method of procedure was similar to that previously described (Trans., 1899, **75**, 471; 1904, **85**, 541).

The values $E^{15^\circ}_{MeOH}$ which we have obtained are as follows:

Acid.		$E^{15^\circ}_{MeOH}$.
Formic	$H\cdot CO_2H$	1124
Acetic	$CH_3\cdot CO_2H$	104
Propionic	$CH_3\cdot CH_2\cdot CO_2H$	91·9
n-Butyric	$CH_3\cdot[CH_2]_2\cdot CO_2H$	50·0
n-Valeric	$CH_3\cdot[CH_2]_3\cdot CO_2H$	53·5
n-Hexoic	$CH_3\cdot[CH_2]_4\cdot CO_2H$	51·5
n-Heptoic	$CH_3\cdot[CH_2]_5\cdot CO_2H$	52·5
n-Octoic	$CH_3\cdot[CH_2]_6\cdot CO_2H$	54·6
n-Nonoic	$CH_3\cdot[CH_2]_7\cdot CO_2H$	53·6
Decoic	$CH_3\cdot[CH_2]_8\cdot CO_2H$	51·8
Lauric	$CH_3\cdot[CH_2]_{10}\cdot CO_2H$	52·9
Myristic	$CH_3\cdot[CH_2]_{12}\cdot CO_2H$	52·5
Palmitic	$CH_3\cdot[CH_2]_{14}\cdot CO_2H$	49·7
Stearic	$CH_3\cdot[CH_2]_{16}\cdot CO_2H$	53·7

The results clearly show the inhibiting effect produced by introducing small radicles, such as methyl and ethyl, into the formic acid molecule. Equally clear is the fact that from butyric acid onwards the rates are very nearly the same for the different acids, so that an increase in the length of the normal chain produces little or no effect on the rate of esterification.

The values obtained for formic and acetic acids are higher than any we have obtained for other acids.

EXPERIMENTAL.

Formic Acid (m. p. 7·8°).

A.—Strength of the hydrochloric acid after mixing = 0·001876 *N.*

15 c.c. of the alcoholic solution required 73·95 c.c. of 0·02692 *N*-baryta.

t in hours.	$a - x$.	$1/t.\log.a/a - x$.
0·2	48·1	0·934
0·3	38·95	0·928
0·36	34·25	0·911

B.—Strength of the hydrochloric acid after mixing = 0·001718 *N.*

15 c.c. of the alcoholic solution required 60·6 c.c. of 0·02692 *N*-baryta.

t in hours.	$a - x$.	$1/t.\log.a/a - x$.
0·2	41·25	0·836
0·3	33·8	0·845
0·4	28·4	0·823
0·5	23·6	0·819

Mean (corrected for *N*-hydrochloric acid) = *A*, 492·7 ; *B*, 483·5.

$$E^{15^\circ}_{MeOH} = 488 \cdot 1 \times 2 \cdot 3026 = \mathbf{1124}.$$

Acetic Acid (m. p. 17°).

A.—Strength of the hydrochloric acid after mixing = 0·008161 *N.*

15 c.c. of the alcoholic solution required 48·54 c.c. of 0·03268 *N*-baryta.

t in hours.	$a - x$.	$1/t.\log.a/a - x$.
0·5	31·45	0·377
0·6	28·57	0·384
0·7	26·95	0·365
0·8	25·05	0·359

B.—Strength of the hydrochloric acid after mixing = 0·01153 *N.*

15 c.c. of the alcoholic solution required 68·03 c.c. of 0·03268 *N*-baryta.

t in hours.	$a - x$.	$1/t.\log.a/a - x$.
0·4	42·4	0·513
0·5	37·95	0·507
0·6	33·58	0·511
0·7	30·85	(0·491)

C.—Strength of the hydrochloric acid after mixing = 0·008146 *N.*

15 c.c. of the alcoholic solution required 55·95 c.c. of 0·02692 *N*-baryta.

t in hours.	$a - x$.	$1/t.\log.a/a - x$.
0·5	36·15	0·379
0·6	33·15	0·379
0·7	30·55	0·375
0·8	28·20	0·372

Mean (corrected for *N*-hydrochloric acid) = *A*, 45·5 ; *B* (first three), 44·3 ; *C*, 46·2.

$$E^{15^\circ}_{MeOH} = 45 \cdot 3 \times 2 \cdot 3026 = \mathbf{104}.$$

Propionic Acid (b. p. 139°/759 mm.).

A.—Strength of the hydrochloric acid after mixing = 0·008214 *N.*

15 c.c. of the alcoholic solution required 46·88 c.c. of 0·03268 *N*-baryta.

t in hours.	$a - x$.	$1/t.\log.a/a - x$.
0·5	32·05	0·330
0·6	29·65	0·333
0·7	27·73	0·326
0·8	25·83	0·324

B.—Strength of the hydrochloric acid after mixing = 0·01270 *N.*

15 c.c. of the alcoholic solution required 47·48 c.c. of 0·03268 *N*-baryta.

t in hours.	$a - x$.	$1/t.\log.a/a - x$.
0·4	29·53	0·516
0·5	26·38	0·510
0·6	23·73	0·502
0·7	21·18	0·501

Mean (corrected for *N*-hydrochloric acid) = *A*, 39·9 ; *B*, 39·9.

$$E^{15^\circ}_{MeOH} = 39 \cdot 9 \times 2 \cdot 3026 = \mathbf{91 \cdot 9}.$$

n-*Butyric Acid* (b. p. 161°/764 mm.).

A.—Strength of the hydrochloric acid after mixing = 0·009659 *N*.

15 c.c. of the alcoholic solution required 46·35 c.c. of 0·03247 *N*-baryta.

t in hours.	$a-x$.	$1/t.\log.a/a-x$.
0·6	34·53	0·213
0·7	32·88	0·213
0·8	31·38	0·212
0·9	29·98	0·210

B.—Strength of the hydrochloric acid after mixing = 0·01474 *N*.

15 c.c. of the alcoholic solution required 46·2 c.c. of 0·03247 *N*-baryta.

t in hours.	$a-x$.	$1/t.\log.a/a-x$.
0·7	27·83	0·314
0·8	25·88	0·315
0·9	24·05	0·315
1·0	22·28	0·317

C.—Strength of the hydrochloric acid after mixing = 0·01474 *N*.

15 c.c. of the alcoholic solution required 46·8 c.c. of 0·03247 *N*-baryta.

t in hours.	$a-x$.	$1/t.\log.a/a-x$.
0·7	27·88	0·321
0·8	25·88	0·322
0·9	24·03	0·322
1·0	22·28	0·322

Mean (corrected for *N*-hydrochloric acid) = *A*, 21·9 ; *B*, 21·4 ; *C*, 21·8.

$$E^{15^\circ}_{\mathrm{MeOH}} = 21{\cdot}7 \times 2{\cdot}3026 = \mathbf{50{\cdot}0}$$

n-*Valeric Acid* (b. p. 185—186·5°).

A.—Strength of the hydrochloric acid after mixing = 0·01307 *N*.

15 c.c. of the alcoholic solution required 46·35 c.c. of 0·03262 *N*-baryta.

t in hours.	$a-x$.	$1/t.\log.a/a-x$.
0·7	28·23	0·308
0·8	26·48	0·304
0·9	24·83	0·301
1·0	23·23	0·300

B.—Strength of the hydrochloric acid after mixing = 0·01307 *N*.

15 c.c. of the alcoholic solution required 46·24 c.c. of 0·03262 *N*-baryta.

t in hours.	$a-x$.	$1/t.\log.a/a-x$.
0·7	28·2	0·307
0·8	26·38	0·305
0·9	24·73	0·302
1·0	22·98	0·304

Mean (corrected for *N*-hydrochloric acid) = *A*, 23·2 ; *B*, 23·3.

$$E^{15^\circ}_{\mathrm{MeOH}} = 23{\cdot}25 \times 2{\cdot}3026 = \mathbf{53{\cdot}5}.$$

n-*Hexoic Acid* (b. p. 199·5—200°/750 mm.).

A.—Strength of the hydrochloric acid after mixing = 0·01307 *N*.

15 c.c. of the alcoholic solution required 45·9 c.c. of 0·03262 *N*-baryta.

t in hours.	$a-x$.	$1/t.\log.a/a-x$.
0·7	28·68	0·292
0·85	26·08	0·289
1·0	23·58	0·289
1·1	21·68	0·296

B.—Strength of the hydrochloric acid after mixing = 0·01307 *N*.

15 c.c. of the alcoholic solution required 45·83 c.c. of 0·03262 *N*-baryta.

t in hours.	$a-x$.	$1/t.\log.a/a-x$.
0·7	28·43	0·296
0·85	25·98	0·290
1·0	23·33	0·293
1·1	21·90	0·292

Mean (corrected for *N*-hydrochloric acid) = *A*, 22·3 ; *B*, 22·4.

$$E^{15^\circ}_{\mathrm{MeOH}} = 22{\cdot}35 \times 2{\cdot}3026 = \mathbf{51{\cdot}5}.$$

n-*Heptoic Acid* (b. p. 223·5—224·5°/772 mm.).

A.—Strength of the hydrochloric acid after mixing = 0·01307 *N*.

15 c.c. of the alcoholic solution required 45·68 c.c. of 0·03262 *N*-baryta.

t in hours.	*a* − *x*.	1/*t*.log.*a*/*a* − *x*.
0·7	28·08	0·302
0·85	25·63	0·295
1·0	23·18	0·295
1·1	21·70	0·294

B.—Strength of the hydrochloric acid after mixing = 0·01305 *N*.

15 c.c. of the alcoholic solution required 45·81 c.c. of 0·03262 *N*-baryta.

t in hours.	*a* − *x*.	1/*t*.log.*a*/*a* − *x*.
0·7	28·05	0·304
0·85	25·60	0·297
1·0	23·15	0·296
1·1	21·65	0·296

Mean (corrected for *N*-hydrochloric acid) = *A*, 22·7 ; *B*, 22·9.

$$E^{15^\circ}_{MeOH} = 22{\cdot}8 \times 2{\cdot}3026 = \mathbf{52{\cdot}5}.$$

n-Octoic Acid (b. p. 231·5—233·5°/765 mm. ; m. p. 14—15°).

A.—Strength of the hydrochloric acid after mixing = 0·0115 *N*.

15 c.c. of the alcoholic solution required 26·43 c.c. of 0·05682 *N*-baryta.

t in hours.	*a* − *x*.	1/*t*.log.*a*/*a* − *x*.
0·5	19·34	0·271
0·6	18·20	0·270
0·7	17·10	0·270
0·8	16·12	0·268

B.—Strength of the hydrochloric acid after mixing = 0·0058 *N*.

15 c.c. of the alcoholic solution required 51·90 c.c. of 0·02888 *N*-baryta.

t in hours.	*a* − *x*.	1/*t*.log.*a*/*a* − *x*.
0·8	40·13	0·140
0·9	38·98	0·138
1·1	36·63	0·138
1·3	34·33	0·138

Mean (corrected for *N*-hydrochloric acid) = *A*, 23·5 ; *B*, 23·9.

$$E^{15^\circ}_{MeOH} = 23{\cdot}7 \times 2{\cdot}3026 = \mathbf{54{\cdot}6}.$$

n-*Nonoic Acid* (b. p. 255—257°).

A.—Strength of the hydrochloric acid after mixing = 0·01174 *N*.

15 c.c. of the alcoholic solution required 52·65 c.c. of 0·02888 *N*-baryta.

t in hours.	*a* − *x*.	1/*t*.log.*a*/*a* − *x*.
0·6	35·85	0·278
0·7	33·60	0·279
0·8	31·70	0·275
0·9	29·80	0·275

B.—Strength of the hydrochloric acid after mixing = 0·018314 *N*.

15 c.c. of the alcoholic solution required 52·43 c.c. of 0·02888 *N*-baryta.

t in hours.	*a* − *x*.	1/*t*.log *a*/*a* − *x*.
0·5	31·98	0·430
0·6	29·20	0·424
0·7	26·73	0·418
0·8	24·45	0·414

Mean (corrected for 0·05 *N*-hydrochloric acid) = *A*, 23·6 ; *B*, 23·0.

$$E^{15^\circ}_{MeOH} = 23{\cdot}3 \times 2{\cdot}3026 = \mathbf{53{\cdot}6}.$$

Decoic Acid (b. p. 270—272°/766 mm. ; m. p. 29—31·5°).

A.—Strength of the hydrochloric acid after mixing = 0·02235 *N*.

15 c.c. of the alcoholic solution required 26·16 c.c. of 0·05682 *N*-baryta.

t in hours.	*a* − *x*.	1/*t*.log.*a*/*a* − *x*.
0·6	13·18	0·496
0·7	11·80	0·494
0·8	10·62	0·489
0·9	9·60	0·484

B.—Strength of the hydrochloric acid after mixing = 0·0115 *N*.

15 c.c. of the alcoholic solution required 26·25 c.c. of 0·05682 *N*-baryta.

t in hours.	*a* − *x*.	1/*t*.log.*a*/*a* − *x*.
0·6	18·20	0·265
0·7	17·14	0·264
0·8	16·22	0·261
0·9	15·37	0·258

C.—Strength of the hydrochloric acid after mixing = 0·006989 *N*.

15 c.c. of the alcoholic solution required 26·48 c.c. of 0·05682 *N*-baryta.

t in hours.	*a* − *x*.	1/*t*.log.*a*/*a* − *x*.
0·6	20·90	0·171
0·75	19·85	0·167
0·9	18·90	0·163
1·1	17·70	0·159

D.—Strength of the hydrochloric acid after mixing = 0·0211 *N*.

15 c.c. of the alcoholic solution required 50·4 c.c. of 0·02692 *N*-baryta.

t in hours.	*a* − *x*.	1/*t*.log.*a*/*a* − *x*.
0·5	29·20	0·474
0·6	26·55	0·464
0·7	23·95	0·462
0·8	21·40	0·465

E.—Strength of the hydrochloric acid after mixing = 0·0103 *N*.

15 c.c. of the alcoholic solution required 50·33 c.c. of 0·02692 *N*-baryta.

t in hours.	*a* − *x*.	1/*t*.log.*a*/*a* − *x*.
0·5	38·18	0·240
0·6	36·28	0·237
0·7	34·43	0·235
0·8	32·68	0·234

F.—Strength of the hydrochloric acid after mixing = 0·01138 *N*.

15 c.c. of the alcoholic solution required 50·33 c.c. of 0·02692 *N*-baryta.

t in hours.	*a* − *x*.	1/*t*.log.*a*/*a* − *x*.
0·5	37·68	0·251
0·8	31·93	0·247
1·3	24·28	0·244
1·8	18·68	0·239

Mean (corrected for *N*-hydrochloric acid) = *A*, 21·95 ; *B*, 22·78 ; *C*, 23·61 ; *D*, 22·09 ; *E*, 22·95 ; *F*, 21·55.

$$E^{15^{\circ}}_{\mathrm{MeOH}} = 22{\cdot}5 \times 2{\cdot}3026 = \mathbf{51{\cdot}8}.$$

Lauric Acid (m. p. 43·5°).

A.—Strength of the hydrochloric acid after mixing = 0·0058 *N*.

15 c.c. of the alcoholic solution required 51·9 c.c. of 0·02888 *N*-baryta.

t in hours.	*a* − *x*.	1/*t*.log.*a*/*a* − *x*.
0·6	42·88	0·138
0·8	40·53	0·134
1·0	38·23	0·133
1·2	36·08	0·132

B.—Strength of the hydrochloric acid after mixing = 0·0058 *N*.

15 c.c. of the alcoholic solution required 51·53 c.c. of 0·02888 *N*-baryta.

t in hours.	*a* − *x*.	1/*t*.log.*a*/*a* − *x*.
0·9	38·93	0·135
1·1	36·78	0·133
1·3	34·73	0·132
1·5	32·83	0·131

Mean (corrected for *N*-hydrochloric acid) = *A*, 23·1 ; *B*, 22·88.

$$E^{15^{\circ}}_{\mathrm{MeOH}} = 22{\cdot}99 \times 2{\cdot}3026 = \mathbf{52{\cdot}9}.$$

Myristic Acid of m. p. 54° (correct m. p. = 53·8°) was used in *N*/30 solution.

A.—Strength of the hydrochloric acid after mixing = 0·01203 *N*.

15 c.c. of the alcoholic solution required 17·4 c.c. of 0·02888 *N*-baryta.

t in hours.	*a* − *x*.	1/*t*.log.*a*/*a* − *x*.
0·6	11·90	0·275
0·7	11·15	0·276
0·9	10·00	0·267
1·0	9·45	0·265

B.—Strength of the hydrochloric acid after mixing = 0·008871 *N*.

15 c.c. of the alcoholic solution required 17·12 c.c. of 0·02888 *N*-baryta.

t in hours.	*a* − *x*.	1/*t*.log.*a*/*a* − *x*.
0·65	12·70	0·200
0·7	12·30	0·205
0·8	11·70	0·207
0·9	11·13	0·208

Mean (corrected for 0·05 *N*-hydrochloric acid) = *A*, 22·5 ; *B*, 23·1.

$$E^{15^{\circ}}_{\mathrm{MeOH}} = 22{\cdot}8 \times 2{\cdot}3026 = \mathbf{52{\cdot}5}.$$

Palmitic Acid of m. p. 62—63° was used in *N*/30 solution.

A.—Strength of the hydrochloric acid after mixing = 0·01211 *N*.

15 c.c. of the alcoholic solution required 15·3 c.c. of 0·03268 *N*-baryta.

t in hours.	*a* – *x*.	1/*t*.log.*a*/*a* – *x*.
0·5	11·32	0·262
0·6	10·67	0·261
0·7	10·02	0·263
0·8	9·47	0·260

B.—Strength of the hydrochloric acid after mixing = 0·01106 *N*.

15 c.c. of the alcoholic solution required 16·8 c.c. of 0·02692 *N*-baryta.

t in hours.	*a* – *x*.	1/*t*.log.*a*/*a* – *x*.
0·5	12·8	0·236
0·3	12·05	0·240
0·7	11·40	0·241
0·8	10·80	0·240

Mean (corrected for *N*-hydrochloric acid) = *A*, 21·6 ; *B*, 21·6.

$$\mathrm{E}^{15^{\circ}}_{\mathrm{MeOH}} = 21{\cdot}6 \times 2{\cdot}3026 = \mathbf{49{\cdot}7}.$$

Stearic Acid of m. p. 69—69·5° was used in *N*/100 solution.

A.—Strength of the hydrochloric acid after mixing = 0·00948 *N*.

15 c.c. of the alcoholic solution required 14·29 c.c. of 0·010175 *N*-baryta.

t in hours.	*a* – *x*.	1/*t*.log.*a*/*a* – *x*.
0·55	10·66	0·231
0·65	10·26	0·221
0·7	10·06	0·218
0·8	9·66	0·213

B.—Strength of the hydrochloric acid after mixing = 0·0212 *N*.

15 c.c. of the alcoholic solution required 11·4 c.c. of 0·01231 *N*-baryta.

t in hours.	*a* – *x*.	1/*t*.log.*a*/*a* – *x*.
0·5	6·40	0·501
0·6	5·80	0·489
0·7	5·15	0·493
0·8	4·55	0·498

Mean (corrected for *N*-hydrochloric acid) = *A*, 23·28 ; *B*, 23·36.

$$\mathrm{E}^{15^{\circ}}_{\mathrm{MeOH}} = 23{\cdot}32 \times 2{\cdot}3026 = \mathbf{53{\cdot}7}.$$

Notes on the Experiments.

1. All the acids used were Kahlbaum's pure acids which had been recently distilled or crystallised. Hygroscopic acids were distilled and collected in receivers which were kept dry by means of phosphoric oxide. After the acid had been weighed, it was kept in a desiccator for several hours before being used.

2. With the higher acids from decoic onwards, flocculent precipitates were obtained when the methyl-alcoholic solutions of the acid were titrated with barium hydroxide, using phenolphthalein as indicator. We made several titrations with the pure acids in order to determine whether the formation of the precipitate interfered with the accuracy of the titration. The experiments proved that very good results can be obtained, even in the presence of a precipitate, provided that the titration is conducted in a good light.

Some of the results we obtained are as follows :

Myristic acid :

20 c.c. of acid solution required 20·45 c.c. of standard baryta.

20 c.c. „ „ „ „ 20·45 c.c. „ „ „

Theory requires 20·44.

Palmitic acid:

0·2563 gram required 30·7 c.c. of standard baryta.
0·2563 gram „ 30·7 c.c. „ „ „
Theory requires 30·66.

3. The higher acids are only sparingly soluble in methyl alcohol at 15°, and hence rather dilute solutions were used in the case of myristic, palmitic, and stearic acids. With the first two acids, *N*/30 and, in the case of the last, *N*/100 solutions were employed.

A saturated solution of stearic acid in methyl alcohol at 15° has a concentration 0·0111 *N*.

4. In the case of the titrations of a mixture of methyl formate and formic acid, the pink coloration persisted for a minute or two only, as the ester was very readily hydrolysed.

5. The values obtained for decoic acid show that the constant tends to decrease with the concentration of the acid more markedly than with the other acids, but the cause of this we have not been able to determine.

We wish to thank the Government Grant Committee of the Royal Society for financial assistance in carrying out this work.

THE EDWARD DAVIES CHEMICAL LABORATORIES,
ABERYSTWYTH.

XXI.—*Studies in Fermentation. Part II. The Mechanism of Alcoholic Fermentation.*

By ARTHUR SLATOR, Ph.D., D.Sc.

IN a previous communication (Trans., 1906, **89**, 128), it was shown that much information concerning the velocity of alcoholic fermentation by living yeast could be obtained by measuring the initial velocity of the reaction under varying conditions. By this means, such disturbing influences as changes in concentration of the reagents, alteration in activity of the yeast, and accumulation of the products of reaction were reduced to a minimum. Solutions containing definite quantities of the reagents were kept at a constant temperature in a closed vessel, which was connected with a manometer. The amount of fermentation which takes place in a short interval of time was measured by change in pressure, owing to the evolution of carbon dioxide. Supersaturation was overcome by vigorous shaking. A number of measurements were given, mainly with the idea of showing the scope of the method of investigation. In the present communication, the fermentation reactions have been much more closely investigated, in the hope of throwing some light on the mechanism of fermentation.

Alcoholic fermentation is probably not a single chemical reaction, but consists of a series, the products of one reaction being the reagents of the succeeding one. The velocity of formation of alcohol and carbon dioxide is determined by the reaction (or reactions) of the series which proceeds slowest.

It is probable that, at higher temperatures (30°), under the conditions of the experiments described here, one single reaction is the main factor in controlling the velocity of evolution of carbon dioxide. The chief use of these velocity measurements is to furnish us with some knowledge of this reaction. The results determine within narrow limits what the reaction is. Velocity measurements can say with almost certainty whether a given compound can be considered an intermediate step in fermentation. Several compounds which have been suggested as such intermediate substances are not in agreement with these experiments.

The Initial Velocity of Fermentation.

The whole of this investigation is a consideration of the initial velocity of fermentation under varying conditions. Living yeast exhibits little abnormality when it starts fermentation, in marked contrast to fermentation by preparations from yeast as "Dauerhefe" or yeast juice. Many problems, such as those now being investigated by A. Harden (*Proc. Roy. Soc.*, 1906, **77**, *B*, 405), cannot be attacked by experiments with living yeast, but a great number of the simpler laws governing fermentation can be much more easily demonstrated by the use of the living organism. Some samples of yeast show the same activity immediately on mixing as they show some hours later. Fresh yeast, mixed with water, retains the same activity for a considerable time. Examples are given in table I. Brewery yeast is mixed with water, the liquid is shaken, and a given volume taken out with a pipette. It is mixed with dextrose solution to give 5 grams of dextrose per 100 c.c. of solution. The rate of evolution of gas from 50 c.c. is measured in the apparatus described in the previous paper. The apparatus has been slightly altered, in that the horizontal tube has been inclined downwards, so that if any liquid froths into this part of the apparatus it runs into the rubber connexion and can be forced back into the bottle.

Whenever it is possible, the solutions are so arranged that readings can be taken every five minutes. Sometimes it is convenient to have enough yeast present to obtain a measurable fermentation every two minutes. When such is the case, an accurate measurement of the velocity can be obtained during the first five minutes after mixing the solutions.

No nutrient salts were added to the solutions, as they have no direct influence on the fermentation. The experiments were mostly carried out at 30°, as the activity of the yeast changes very slowly at this temperature. One cm. on the manometer scale corresponds with a fermentation of approximately 8 milligrams of dextrose.

TABLE I.

Temperature 30°.	Velocity in cm. per 10 mins.
On mixing yeast and dextrose solution	14·0
After 2½ hours	14·4
On mixing yeast and dextrose solution	10·7
After 35 minutes	10·3
Activity of fresh yeast	7·2
On standing overnight at 15°	7·1

Sometimes specimens of yeast show a somewhat varying activity during the first half-hour of fermentation, and then the reaction becomes steady and proceeds at a constant velocity for several hours. Throughout this investigation only comparative experiments have been made, and, when only one variable (such as concentration or temperature) is altered at a time, there is no difficulty in obtaining comparative results. The pure yeast used in some of the experiments was obtained by inocculating ordinary sterile, lightly hopped brewers' wort of sp. gr. 1·040 with the culture, and allowing the growth and fermentation to continue for about a week.

Many of the cultures of yeast used in these experiments were a present from Mr. A. C. Chapman and Mr. F. G. S. Baker, to whom I desire to express my indebtedness.

The Fermentation of Lævulose.

According to various investigations, the rates of fermentation of dextrose and lævulose show differences depending on the conditions of the experiments and the variety of yeast used (for a summary of these experiments see Lippmann, "Die Chemie der Zuckerarten," p. 866). It is probable that the differences observed are due to the growth or to changes in activity of the yeast during the time of the experiment, for, if such influences are eliminated, the rates of fermentation of dextrose and lævulose are found to be almost identical.

The experiments were carried out in the following way. The yeast to be investigated was grown in wort under sterile conditions, washed by decantation with cold water, and finally shaken with water. Twenty-five c.c. of the mixture were added to 25 c.c. of a solution of dextrose containing 10 grams of sugar per 100 c.c., and the velocity of formation of carbon dioxide was measured. A similar experiment was carried out, replacing the dextrose by lævulose. A comparison of the two velocities gives the ratio of the rate of fermentation of the two sugars. Table II shows that this ratio, *R*, is approximately 1. Similar experiments with 5 per cent. invert sugar show that the mixture of the two sugars also ferments at approximately the same rate as dextrose.

TABLE II.

The Comparative Velocity of Fermentation of Dextrose and Lævulose.

Yeast.	Ratio *R*. Dextrose	:	Lævulose	:	Invert sugar.
Saccharomyces cerevisiæ	100	:	93	:	106
,, *exiguus*	100	:	102		
,, *Thermantitonum*	100	:	106		
,, *ellipsodeus*	100	:	105		
,, *Carlsberg* 1	100	:	105		
,, *apiculatus* (*Reess*)	100	:	105		
Schizosaccharomyces Pombe	100	:	111		
Kefir yeast	100	:	91		
Zymin *	100	:	97		
Hefenol *	100	:	100		

* Dry preparations of yeast (see later).

If brewery yeast is partly destroyed by various reagents, the crippled yeast also ferments dextrose and lævulose at the same rate.

TABLE III.

Destroying agent.	Percentage of the activity destroyed.	Ratio *R*. Dextrose	:	Lævulose.
Heat	41	100	:	100
Alcohol	42	100	:	99
Iodine	40	100	:	99
Alkali	35	100	:	93

In all probability, all yeasts and preparations from yeast ferment dextrose and lævulose at the same rate.

Experiments were also carried out to measure the influence of concentration and temperature on the rate of fermentation of lævulose. The results are included in tables X and XI. As in the case of the fermentation of dextrose, the concentration of the sugar has little influence on the rate of fermentation. The influence of temperature is practically identical with that on the rate of the fermentation of dextrose.

These experiments show that lævulose can replace dextrose in a fermenting solution without any change in the velocity of evolution of carbon dioxide. When we consider how sensitive the velocity of chemical reactions, especially enzyme reactions, are to changes of conditions, the practical identity of these two reactions is very significant. It is possible, but not very probable, that the reaction which is measured in these experiments is one independent of the sugar entirely, the sugar being involved in some other reaction which takes place later, and that this second reaction proceeds so rapidly that it has no controlling influence on the evolution of carbon dioxide. Another explanation may be suggested, namely, that dextrose and lævulose form the same substance, and that the controlling reaction involves this substance in such a way that the velocity is the same whether dextrose or lævulose is used in the experiment. For instance, it has been suggested that the first step in fermentation is the formation of the enolic form of the sugar. The enolic forms of dextrose and lævulose are the same, and here, at first sight, seems a possible explanation of the above results. On further consideration, difficulties appear. If we consider the three equilibria: (1) $D \rightleftharpoons X$, (2) $L \rightleftharpoons X$, (3) $D \rightleftharpoons L$ or $D \rightleftharpoons X \rightleftharpoons L$, where D and L represent dextrose and lævulose respectively, and X a substance such as the enolic form of the sugars, then it is easy to show that the time to establish the equilibrium (3) is of the same order as the time to establish the two equilibria (1) and (2). When dextrose or lævulose is dissolved in water, equilibrium (3) is not established.* There is no indication of the transformation of dextrose to lævulose in neutral or slightly acid solutions, and therefore the reactions $D \longrightarrow X$ and $L \longrightarrow X$ must proceed exceedingly slowly in these solutions, so slowly that it is impossible to consider them steps in the fermentation reaction. If X is an intermediate compound in the reaction, the following conditions must be fulfilled: the reactions $D \longrightarrow X$, $L \longrightarrow X$ must proceed rapidly, the opposite reactions $X \longrightarrow D$, $X \longrightarrow L$ must proceed slowly, and the quantity of X present at any given time must be very small. These conditions are satisfied if we consider X to be a compound between the sugar and the enzyme, and with certain suppositions we can construct a step in the fermentation of dextrose and lævulose which is in argeement with the velocity experiments and is not, so far as can be seen, contradicted by any of the known properties of the reaction. The assumptions are that the whole of the enzyme is combined with the dextrose or lævulose, that the compound formed in each case is the same, and that there is no appreciable decomposition of the compound back again to dextrose and lævulose.* The two important results explained by such a hypothesis are that the velocity of fermentation is independent of the concentration of the sugar between certain limits, and that dextrose and lævulose ferment at the same rate. There is no difficulty in constructing such a compound, but a discussion of its nature is reserved until the results of the measurements of the velocity of fermentation of galactose and mannose are described.

---

* It is assumed by T. M. Lowry that when dextrose dissolves in water the proportion of the enolic form is exceedingly small, and that the small concentration prevents the rapid establishment of the equilibrium $D \rightleftharpoons L$ (Trans., 1904, **85**, 1565). A small equilibrium concentration of the enolic form is no bar whatever to the transformation of dextrose into lævulose. It must be assumed that when dextrose is dissolved in water the amount of enol formed is approximately as small compared to its concentration when the equilibrium $D \rightleftharpoons X$ is established as the amount of lævulose formed is to its concentration when the equilibrium $D \rightleftharpoons L$ is established.

This hypothesis is also in agreement with results obtained from experiments with invert sugar. Invert sugar ferments at the same rate as dextrose and lævulose. The evolution of carbon dioxide depends on the quantity of the compound X present, and this amount is the same whether it is formed only from dextrose or only from lævulose, or from both.

That dextrose and lævulose ferment at the same rate in separate solutions does not necessarily mean that, during the fermentation of invert sugar, dextrose and lævulose disappear at the same rate. In some cases, a residue rich in lævulose is obtained after partial fermentation, and under other conditions the lævulose disappears faster than the dextrose (Lippmann, *loc. cit.*, p. 934). The relative rate of the two fast reactions $D \longrightarrow X$ and $L \longrightarrow X$ is the determining factor which settles whether a preponderance of dextrose or lævulose disappears in the first part of he fermentation of invert sugar. We need only suppose a change in the relative rate of the two reactions by a variation in the conditions of the experiments to afford a plausible explanation of the varying results obtained by different investigations. It is improbable that the somewhat different rates of diffusion of dextrose and lævulose into the cell play any important part in determining whether dextrose or lævulose disappears the faster from the solution (compare Prior and Schultz, *Zeitsch. angew. Chem.*, 1901, **14**, 208).

The Fermentation of Galactose.

Numerous investigations (see Lippmann, *loc. cit.*, p. 734) which have been carried out in connexion with the action of yeast on galactose show that there is a considerable difference in the fermentation of this sugar compared with that of dextrose and lævulose. In the first place, all yeasts do not ferment this sugar, and, further, those that have this property possess it only after the yeast has become "acclimatised" by growing in the presence of the sugar. Most varieties of yeast act less vigorously on galactose than on dextrose, although a few yeasts are described which ferment galactose more rapidly than dextrose. Experiments with a large number of yeasts lead E. F. Armstrong (*Proc. Roy. Soc.*, 1905, *B*, **76**, 600) to conclude that the fermentations of dextrose and galactose are brought about by different mechanisms.

---

* The fact that the equilibrium $D \rightleftharpoons L$ is not rapidly established, although the sugars quickly form a compound with the enzyme which is the same in each case, may perhaps be made clearer by the following example. When a little phenylhydrazine is added to a dextrose solution, a small quantity of osazone may be formed, which is the same osazone as that formed when a similar experiment is carried out with lævulose and phenylhydrazine. At the same time, phenylhydrazine does not act as a catalytic agent rapidly establishing the equilibrium $D \rightleftharpoons L$.

In this investigation, the acclimatisation of the yeasts was first verified. It was found that ordinary brewery yeast had no action on galactose. The specimen of galactose (Kahlbaum's) used in the first experiments contained a small quantity of dextrose, for on submitting the sugar to the action of yeast in the apparatus a small fall in pressure was noticed. In a short time, the whole of the impurity had disappeared, and the evolution of gas was merely due to the autofermentation of the yeasts (compare Armstrong). The galactose solution was easily freed from fermentable substances by treatment with brewery yeast.

Experiments were then carried out with some pure yeast cultures. Two growths of *S. Carlsberg* 1 were obtained, one by growth in ordinary malt wort of sp. gr. 1·040, and the other in a solution of hydrolysed lactose (dextrose and galactose) to which a small quantity of wort had been added to supply the necessary food for the yeast. The yeast crop was in each case washed by decantation with cold water, and the activity of the yeast estimated in the same way as that used in the investigation of lævulose. The rate of fermentation of 2½ per cent. dextrose was compared directly with that of 2½ per cent. galactose. In the cases where the rate of fermentation of galactose was very small, a correction was made for the autofermentation of the yeast.

Figures given in table IV show that yeast grown in wort is incapable of fermenting galactose, the rate of fermentation of dextrose being at least one hundred times greater than that of galactose. Yeast grown in the second solution ferments this sugar with a velocity comparable with that of the fermentation of dextrose.

A number of experiments were carried out with other varieties of yeasts and with various growths. The results are summarised in the second part of the table.

TABLE IV.

The Acclimatisation of Yeasts to Galactose.

S. Carlsberg 1 grown in wort.

Autofermentation	0·15 cm. per 10 mins.
2½ per cent. galactose	0·10 ,, ,,
2½ ,, dextrose	4·00 ,, ,,

Ratio $R=100:<1$.

S. Carlsberg 1 grown in hydrolysed lactose.

2½ per cent. galactose	6·3 cm. per 10 mins.
2½ ,, dextrose	7·3 ,, ,,

Ratio $R=100:86$.

Yeast.			Ratio *R*.		
			Dextrose	:	Galactose.
S. Carlsberg 1	grown in	wort	100	:	<1
,,	,,	hydrolysed lactose	100	:	86, 83, 85, 25, 46 51, 69, 54, 155
S. cerevisiæ	,,	wort	100	:	<1
,,	,,	hydrolysed lactose	100	:	21, 26, 29
S. Thermantitonum	,,	wort	100	:	<1
,,	,,	hydrolysed lactose	100	:	77, 53, 35
S. Ludwigii	,,	wort	100	:	<1
,,	,,	hydrolysed lactose	100	:	<1

From this table, it is seen that yeasts grown in solutions which do not contain galactose have not the property of fermenting this sugar. Some acquire this property on growing in the presence of galactose. The ratio *R* varies greatly with the conditions of growth; thus growths of *S. Carlsberg* 1 have been obtained which give values varying between 100 : 0 and 100 : 155. The influence of various conditions on this factor have not yet been studied.

These experiments suggest many problems in connexion with this sugar.

It has been found possible to acclimatise a yeast so that it ferments galactose half as fast again as dextrose; it would be of interest to find if yeasts could be acclimatised still further, and what the limit of activity to galactose is. Again, can yeasts, which are considered incapable of fermenting galactose, be made to acquire this property after successive growths in the presence of this sugar? In investigations on such lines, measurements of the ratio *R* would be of much value. This ratio may also serve as a help in the identification of different varieties of yeast.

If a given variety of yeast, which is quite incapable of fermenting galactose, acquires this property even after one growth in the presence of this sugar, it is conceivable that some varieties of yeast may be trained to ferment sugars which have so far been considered unfermentable.

The incapability of yeasts of fermenting galactose before acclimatisation will explain nearly all the conflicting results which have been obtained in various investigations of the fermentation of this sugar. One example will suffice. A yeast has been described by Fischer and Thierfelder (*Ber.*, 1894, **27**, 2031) which ferments galactose only partly, but ferments lactose entirely. The yeast evidently contains the enzyme lactase. It is more easily acclimatised when grown in the presence of dextrose and galactose than when galactose only is present; hence the curious result that this yeast ferments lactose more readily than galactose.

The effect of variations of concentration of galactose, and change in temperature on the velocity of fermentation, are included in tables X and XI.

It is evident that considerable differences exist in the way galactose and dextrose are fermented, and it might almost be thought that they are two separate and distinct reactions, possibly brought about by different enzymes. It is, however, easily shown that this is not entirely the case. If these two reactions were quite distinct, and no interference between them took place, the rate of evolution of carbon dioxide from the fermentation of a mixture of the two sugars would be the sum of the rates of the two singly. Experiments with 2½ per cent. sugar solutions show that this is not the case. The rate of fermentation of a solution of 2½ per cent. dextrose and 2½ per cent. galactose is very considerably below the sum of the rates of the two reactions measured singly, and is usually somewhat higher than the rate of fermentation of 2½ per cent. dextrose. The dextrose is the main factor in determining the velocity of reaction. This is specially brought out in the experiment with yeast which is more reactive to galactose than dextrose. An addition of dextrose to the fermenting galactose causes an appreciable diminution in the velocity of evolution of gas. The results are given in table V. The yeast was in each case grown in hydrolysed lactose solution and washed by decantation with water. The rate of fermentation of dextrose is called 100, in order to easily compare the different experiments. It has been previously shown that yeast which has been partly destroyed still ferments dextrose and lævulose at approximately the same rate (table II). Similar experiments were carried out with dextrose and galactose. The ratio *R* was measured for a given specimen of yeast, the yeast was partly destroyed by heat or by treatment with alcohol, and the ratio again measured. The results are also included in table V. They show that the ratio *R* may alter considerably when the yeast has undergone such treatment.

TABLE V.

The Simultaneous Fermentation of Dextrose and Galactose.

Yeast.	Ratio *R*.		
	Dextrose	: Galactose	: Dextrose + Galactose.
S. cerevisiæ	100 :	0 :	103
,, ...	100 :	34 :	103
S. Carlsberg 1	100 :	96 :	110
,, ...	100 :	155 :	119
S. Thermantitonum............	100 :	76 :	124

The Effect of Inhibiting Agents on the Ratio R.

Inhibiting agent.	Percentage activity destroyed.	Ratio *R*.	
		Before treatment.	After treatment.
Heat ...	36 per cent.	100 : 69	100 : 78
,, ...	40 ,,	100 : 51	100 : 54
,, ...	64 ,,	100 : 50	100 : 32
,, ...	90 ,,	100 : 97	100 : 54
Alcohol.	23 ,,	100 : 80	100 : 80
,,	42 ,,	100 : 97	100 : 68

In the fermentation of maltose (described later), it was found possible to detect an accumulation of fermentable intermediate compound (dextrose) by adding to the fermenting solution a yeast which is capable of fermenting dextrose and not maltose. It is unlikely that during the fermentation of galactose a similar accumulation takes place, but it was considered worth while carrying out the experiment. Brewery yeast does not ferment galactose, and hence can be used as a reagent to detect the accumulation of an easily fermentable compound. The rate of fermentation of galactose was therefore measured without and in the presence of brewery yeast. The increase in velocity in the latter case is too small to be of any account. From this experiment and also from a consideration of the results of the other measurements, we can be fairly certain that galactose is not transformed to another fermentable sugar (as dextrose) before fermentation.

TABLE VI.

The Fermentation of Galactose in the Presence of Brewery Yeast

Solution.	Velocity.
25 c.c. *S. Carlsberg* 1 + 25 c.c. 5 per cent. galactose	5·3 cm. per 10 mins.
,, ,, + 3 c.c. brewery yeast	5·9 ,, ,, ,, ,,
After standing 1 hour	5·1 ,, ,, ,, ,,
25 c.c. *S. Thermantitonum* + 25 c.c. 5 per cent. galactose...	6·35 ,, ,, 15 ,,
,, ,, + 5 c.c. brewery yeast	6·80 ,, ,, ,, ,,

Galactose is not fermented by "Dauerhefe," and only slightly by yeast juice. Experiments with preparations from acclimatised yeast have not yet been carried out.

The Fermentation of Mannose.

Mannose, according to a number of investigations, is fermented regularly and completely by almost all yeasts (possibly all yeasts) which ferment dextrose. Measurements of the initial velocity of fermentation of this sugar show that no treatment of the nature of acclimatising the yeast is necessary to bring about the reaction. The velocity is dependent on the variety of yeast and the treatment the yeast has received. Fresh samples of yeast ferment mannose more quickly than dextrose, but with older samples the rate of evolution of carbon dioxide is faster with dextrose than with mannose. This is specially the case with yeast which has been partly destroyed by heat.

TABLE VII.

The Comparative Velocity of Fermentation of Dextrose and Mannose.

Yeast.	Ratio *R*.				
	Dextrose	:	Mannose	:	Dextrose + Mannose.
S. Carlsberg 1	100	:	124		
S. Thermantitonum	100	:	105	:	92
Kefir yeast	100	:	147		
Brewery yeast	100	:	120		
,, (grown in the presence of mannose)	100	:	123		
,, old	100	:	84		
,, 22 per cent. activity destroyed by heat	100	:	35		
,, 53 per cent. activity destroyed by heat	100	:	21	:	33
,, 60 per cent. activity destroyed by heat	100	:	12	:	42

In the experiments summarised in this table, the rates of fermentation of 2½ per cent. dextrose, 2½ per cent. mannose, and 2½ per cent. dextrose + 2½ per cent. mannose are compared. The results show that when the two sugars are fermented simultaneously, interference between the reactions takes place. Mannose seems to retard the velocity of fermentation of dextrose. This is specially evident in the case where the yeast has comparatively little action on mannose.

The influence of concentration of the sugar and the influence of temperature have also been measured. The results are included in tables X and XI.

The variation in the ratio *R* for a given culture of yeast will, in all probability, explain the disagreement in the literature with regard to capability of certain yeasts of fermenting mannose. Thus *S. exiguus* and *S. Pombe*, according to P. Lindner, do not ferment mannose, whilst, according to E. F. Armstrong, these two yeasts ferment mannose apparently as easily as dextrose. It is evident that a quantitative measurement of the rate of fermentation in the manner described in this paper would be of much value in determining whether a given yeast ferments a given sugar or not.

The Fermentation of Disaccharides.

It is generally accepted that poly- and di-saccharides are not directly fermented by yeast, but are first hydrolysed by enzymes to fermentable sugars.

The rate of fermentation of a disaccharide therefore depends on this rate of hydrolysis.

In the case of sucrose, this hydrolysis proceeds so quickly that enough dextrose and lævulose is immediately formed for the fermentation reaction to attain its maximum velocity.

In the fermentation of such substances as glycogen (autofermentation), dextrin, and others which ferment slowly, the rate of hydrolysis is the controlling factor which governs the rate of fermentation.

In the former case, the intermediate product (invert sugar) is easily detected in the solution; in the latter case, the intermediate sugar (dextrose) is fermented away as fast as it is formed, and cannot be isolated without treating the yeast in such a way as to destroy the enzyme of fermentation and leave the hydrolytic one.

The fermentation of maltose by brewery yeast affords an interesting case where the rate of hydrolysis of the maltose and the rate of fermentation of the ensuing dextrose are very similar. At low temperatures, the initial rate of fermentation of maltose is appreciably lower than that of dextrose, whilst at higher temperatures the two velocities are almost the same.

TABLE VIII.

Temperature.	Ratio, 5 per cent. solutions. Dextrose : Maltose.
15°	100 : 68
30	100 : 90

This is also confirmed by the measurements of the temperature-coefficient of the fermentation of maltose. The influence of temperature is considerably greater than that on the fermentation of dextrose, especially at lower temperatures (see table XI). It is evident that when maltose ferments, some dextrose probably accumulates in the solution. The accumulation is too small to admit of an easy direct proof, but evidence of its formation can be obtained in the following way. If to a solution containing maltose and yeast another yeast is added which is incapable of fermenting maltose, but reacts with dextrose, an increase in the rate of evolution of carbon dioxide should indicate the presence of dextrose. *S. exiguus* was used for this purpose, as it ferments dextrose easily, but not maltose. The fermentation of maltose carried out in the presence of this yeast shows initially very little difference to that without the yeast, but after standing three hours a considerable increase in the rate of evolution of gas is noticed. The initial rate of fermentation of a solution of maltose is practically the same as that after three hours, the increase is therefore due to the presence of *S. exiguus*.

TABLE IX.

Fermentation of Maltose in the Presence of S. exiguus.

Temperature, 30°. Volume, 50 c.c.

Solution.	Velocity.
5 c.c. brewery yeast, 5 per cent. maltose	7·4 cm. per 20 mins.
25 c.c. *S. exiguus* (autofermentation)	1·8 ,, ,,
5 c.c. brewery yeast, 25 c.c. *S. exiguus*, 5 per cent. maltose	8·55 ,, ,,
Ditto, after 3 hours	14·45 ,, ,,
Correction for autofermentation	1·8 ,, ,,
	12·65 ,, ,,
Increase from 7·4 to 12·65 = 71 per cent. increase.	
Another experiment gave 52 ,, ,,	
Initial rate of fermentation of maltose by brewery yeast	7·0 cm. per 5 mins.
After 3 hours	7·2 ,, ,,

The Influence of Concentration and Temperature on the Rate of Fermentation of Various Sugars.

The influence of the concentration of the sugar, and the influence of temperature on the rates of reaction of the various sugars, are conveniently summarised in the two following tables. In table X the different velocities at different concentrations are recalculated, making the velocity of a 5 per cent. solution 100. The equivalent of 100 is given in the table in cm. per ten minutes on the manometer scale. The activity of the yeast as measured by the ratio R is also included. In all cases except at dilute solution, the velocity is approximately independent of the concentration of the sugar.

TABLE X.

The Influence of Concentration of Sugar.

	Velocity.			
Grams of sugar per 100 c.c.	Dextrose.	Lævulose.	Galactose.	Mannose.
0 per cent. (autofermentation)	—	6	3	5
½ ,, ,,	87	73	79	63
1 ,, ,,	92	93	88	88
2½ ,, ,,	98	106	92	105
5 ,, ,,	100	100	100	100
10 ,, ,,	94	106	102	95
The equivalent of 100 in cm. per 10 mins.	5·4	7·0	2·9	7·7
Ratio *R*	—	100 : 93	100 : 85	100 : 79

Table XI gives the temperature quotients for the different sugars. The experiments were carried out in the manner described in the previous paper, with the exception of those with sucrose and maltose. In these cases, initial velocities with different solutions at different temperatures were measured. The yeast exhibited no abnormal initial velocities, and there was no need to correct for changes in activity of the yeast. Brewery yeast was used in all cases except in the fermentation of galactose. A growth of *S. Carlsberg* 1 in hydrolysed lactose was used to ferment this sugar.

TABLE XI.

Temperature Quotients with Different Sugars.

V_{t+5}/V_t.	Dextrose.		Lævulose.	Sucrose.	Maltose.	Galactose.	Mannose.
V_{10}/V_5	2·5	—	2·6	—	—	1·94	—
V_{15}/V_{10}	1·98	—	1·93	2·12	2·7	1·72	—
V_{20}/V_{15}	1·91	1·97	1·82	1·90	2·5	1·59	1·78
V_{25}/V_{20}	1·60	1·60	1·52	1·58	1·96	1·37	1·58
V_{30}/V_{25}	1·44	1·53	1·45	1·36	1·50	1·34	1·35
V_{35}/V_{30}	1·35	1·25	1·32	1·24	1·33	1·25	1·34
V_{40}/V_{35}	1·25	1·15	1·24	1·16	1·32	1·10	1·21

The second series of figures under dextrose are obtained with the yeast *S. Thermantitonum*, a yeast which exerts its maximum fermentative power at as high a temperature as 45° (Grove Johnson, *J. Inst. Brewing*, 1905, **11**, 466). This property has no connexion with the influence of temperature on alcoholic fermentation, which is approximately independent of the variety of yeast used to bring about the reaction (Trans., 1906, **89**, 137).

Intermediate Compounds in the Fermentation of Dextrose.

The following substances have been suggested as intermediate compounds in the conversion of dextrose into alcohol and carbon dioxide by yeast:

(1) The enolic form of dextrose (E. F. Armstrong, *loc. cit.*).

(2) Lactic acid (Buchner and Meisenheimer, *Ber.*, 1905, **38**, 620).

(3) Glycogen (Kohl, *Annales de la Brasserei*, 1907, 306).

These velocity measurements are very much opposed to the acceptance of any of these suppositions. The first suggestion has been already discussed (p. 221).

In previous publications (Trans., 1906, **89**, 141; *Ber.*, 1907, **40**, 123), it has been shown that it is very improbable that lactic acid can be considered such a substance. It is doubtful whether lactic acid is fermentable; in no circumstances is it possible to ferment lactic acid as fast as dextrose, and the inhibiting action of the acid is not sufficient to explain its very slow rate of fermentation. Evidence in favour of this last statement is obtained as follows: 50 c.c. of yeast and water are treated in the apparatus successively with lactic acid and then dextrose, and measurements are made after each addition. The second measurement is much greater than the first, showing that yeast which is almost incapable of fermenting lactic acid still possesses the property of rapidly fermenting dextrose.

TABLE XII.

Solution-temperature 30°.	Velocity.
50 c.c. yeast + water + ½ gram lactic acid	0·30 cm. per 2 mins.
Same solution + ½ gram dextrose	4·00 ,, ,,

The first velocity is probably entirely due to autofermentation, but if it were caused wholly by the fermentation of lactic acid the experiment would still be conclusive in showing that the inhibiting effect of the acid is not enough to account for its slow rate of fermentation. This experiment was carried out at the suggestion of Prof. Buchner to afford better evidence than that given in a former paper. (See table I, *Ber.*, 1907, **40**, 124.)

It has also been suggested that an unknown isomeride of lactic acid is such an intermediate compound, and that traces of lactic acid are formed from this isomeride (Luther, *Zeitsch. Elektrochem.*, 1907, **13**, 516).

The assumption that lactic acid is a by-product from an intermediate compound which is arbitrarily called an isomeride of this acid has little experimental basis. We have nothing to decide us from what compound the traces of lactic acid are formed. The main evidence in favour of this supposition is probably the ease with which the chemical equations, dextrose ⟶ lactic acid ⟶ alcohol and carbon dioxide, can be constructed.

Glycogen has also been suggested as the first transformation product of dextrose before fermentation. On the assumption that the autofermentation of yeast is caused by the presence of glycogen in the yeast cell, it is very difficult to bring into agreement the above supposition and the few experiments which have been carried out here.

The rate of autofermentation is only some few per cent. of that of dextrose. When a very small quantity of sugar is added to excess of yeast at 30°, the whole of the sugar is fermented away in about twenty minutes, and the original rate of autofermentation is again observed.

TABLE XIII.

Time.	Manometer reading.	Velocity in cm. per 10 mins.
0 min.	1·2	—
10 mins.	2·2	1·0 (autofermentation)
0·1 gram dextrose added.		
15 ,,	7·8	11·2
20 ,,	13·9	12·2
30 ,,	16·7	2·8
40 ,,	17·75	1·05 (autofermentation)

It is hardly reasonable to think that the whole of the sugar has passed through the glycogen stage, or that the slow fermentation of glycogen is an essential part of the rapid fermentation of dextrose.

Many of the other velocity measurements could be urged against this supposition.

In conclusion, it may be again pointed out that no compound has yet been isolated which is likely to prove an intermediate step in the fermentation reaction. It is probable that such a compound would be very unstable, easily fermented, and hard to isolate.

The method of adding a reagent to react with the unstable intermediate compound is often useful in detecting such substances. Löb (*Zeitsch. Elektrochem.*, 1907, **13**, 511) has applied this method to detect aldehydic compounds during fermentation, using phloroglucinol, ammonia, and aniline for the purpose. The results were negative.

The Influence of Substances which are said to accelerate Fermentation.

In the literature of the fermentation of dextrose, one finds numerous investigations on the action of "poisons," that is, substances which when present in a fermenting solution in dilute concentration retard the reaction. It is also stated that many of these poisons in very dilute solution have the opposite effect of accelerating alcoholic fermentation.

Examples of such substances are mercuric chloride, iodine, potassium iodide, salicylic acid, benzoic acid, sulphuric acid, and potassium permanganate (for complete list, see Lippmann, *loc. cit.*, p. 395). At very dilute concentration, they accelerate alcoholic fermentation, and in more concentrated solution they inhibit the reaction. On applying the method used in this investigation, it was found that, although the retardation effect could easily be verified, no appreciable accelerating effect on fermentation could be shown by any of these reagent. In all probability, the effect which has previously been attributed to the acceleration of alcoholic fermentation is due to the acceleration of some other reaction (as the growth of yeast) which the method of investigation has not eliminated. In a few cases, a slight increase was observed, but this is too small to be of any importance in these measurements.

The following table shows the effect of four poisons. The concentrations which are said to accelerate the reaction are given in brackets. The table also includes a comparison of the rate of fermentation of dextrose with that of unhopped brewery wort of sp. gr. 1·030. The latter contains, besides sugars, very favourable food material for the growth of the yeast. The initial velocities are almost identical.

TABLE XIV.

Temperature, 30°.

Poison.	Concentration.	Velocity.
Potassium iodide (1/100,000)	1/00	100
	1/300,000	98
	1/150,000	103
	1/30,000	100
Iodine (1/600,000)	1/00	100
	1/500,000	99
	1/100,000	97
	1/50,000	76
Salicylic acid (1/4000—1/6000)	1/00	100
	1/50,000	94
	1/10,000	98
	1/5000	60
	1/2000	4
Copper sulphate, $CuSO_4,5H_2O$ (1/600,000)	1/00	100
	1/500,000	95
After standing 4 hours		90
	1/50,000	50 (rapidly decreasing)

Rate of fermentation of 7 per cent. dextrose	100
,, ,, wort sp. gr. 1·030	106

M. Delbrück in a recent paper (*J. Inst. Brewing*, 1906, **12**, 654) states that ground oats accelerate alcoholic fermentation. From 400 c.c. of a 10 per cent. sucrose solution with 10 grams of pressed yeast and 5 grams of crushed oats, he obtains double the volume of carbon dioxide in four hours as from the sugar solution and yeast alone.

The following table shows that the result is not confirmed by this method of investigation. It can only be suggested that some error lies in the estimation of the rates of fermentation where supersaturation takes place.*

TABLE XV.

The Influence of Ground Oats on Fermentation.

Temperature, 30°. Solution.	Velocity in cm. per 6 mins.
50 c.c. 10 per cent. sucrose	5·0
,, ,, ,, +0·5 gram oats	4·85
,, ,, ,, +1 ,, ,,	4·55
,, ,, ,, +4 ,, ,,	3·0
,, ,, ,,	8·45
,, ,, ,, +0·63 gram oats (on mixing)	7·8
,, ,, ,, ,, ,, ,, (1½ hours later)	6·1

The first experiment, where increasing quantities of oats are added to 50 c.c. of 10 per cent. sucrose and yeast, shows only a retarding effect of this substance. The second experiment, which is made to agree as nearly as possible with Delbrück's, shows that on standing the velocity does not increase.

It has been shown that there is a large acceleration in the velocity of evolution of carbon dioxide when neutral soluble phosphates are added to a dextrose solution which is undergoing fermentation by "yeast juice" or by permanent yeast cells (A. Harden and W. J. Young, *Proc. Roy. Soc.*, 1906, **77**, *B*, 405). There is no doubt of this acceleration, but phosphates have no accelerating influence on the rate of fermentation by living yeast (see table XVII).

In conclusion, it may be stated that we have not yet succeeded in finding a substance which will appreciably accelerate fermentation by fresh living yeast.

Fermentation by Preparations from Yeast.

In view of the fact that the laws which underlie alcoholic fermentation by living yeast are comparatively simple, a few measurements were made with the preparation from yeast known as "Dauerhefe," which, according to R. O. Herzog (*Zeitsch. physiol. Chem.*, 1902, **37**, 149), gives results differing from those described here in many respects.

It was found that these differences are mainly due to disturbing secondary reactions which take place when this preparation from yeast acts on a sugar solution. The laws which govern the fermentation reaction by living yeast and by the "Dauerhefe" are essentially the same, but, owing to these secondary reactions, they are in the latter case much more difficult to recognise.

---

* Whatever method is used to estimate the activity of yeast, it should only be accepted as trustworthy when it can show that exact proportionality exists between the rate of fermentation and quantity of yeast added (compare Trans., 1906, **89**, 131).

The preparation which is used in all these experiments was made by Anton Schroder, Munich, who sells the product under the name of "zymin."

On testing the specimen, it was found that the enzyme is at first quite inactive; after an induction period of between one and two hours, the reaction starts vigorously, it soon attains a maximum velocity, slows down considerably, and then proceeds steadily, gradually diminishing in velocity.

The following tables show that dextrose and lævulose ferment at the same rate (*C* and *D*), the concentration of the sugar has little influence on the velocity (*C* and *E*), that the autofermentation is appreciable (*A* and *C*), and allowing the "zymin" to stand with water before adding the sugar greatly reduces the period of induction.

The addition of neutral potassium phosphate has an accelerating effect both on the autofermentation (*A* and *B*) and also on the fermentation of dextrose and invert sugar (table XVII).

An accelerating effect is also produced when a boiled solution of "zymin" is added to some fresh "zymin" (*G* and *H*). According to Herzog's measurements, when double the amount of "zymin" is present in a solution the reaction proceeds four times as fast, but it is evident that the large increase in velocity is only partly due to doubling the amount of enzyme, for at the same time a further quantity of accelerating agent is added.

Another dry preparation of yeast, "hefenol," gave quite analogous results, showing an induction period and increased activity in the presence of phosphates. Living yeast is not rendered more active by phosphates, but preparations, such as "zymin," "hefenol," yeast juice, react more vigorously under the influence of these salts. It is of interest to find what treatment the yeast must undergo to show this property. Products obtained by partly killing the yeast by heat or by alcohol were not sensitive in this manner. On the other hand, by drying the yeast at a low temperature, a preparation was produced which was much more active in the presence of phosphates (table XVIII). The extraction of water is possibly the main factor in rendering the enzyme sensitive to phosphates.

TABLE XVI.

Fermentation by Zymin (Acetondauerhefe).

t = Time in minutes.

Solution A = 50 c.c. water + 5 grams zymin.
,, B = ,, ,, + ,, ,, + 5 c.c. phosphate solution.
,, C = ,, 5 per cent. dextrose + 5 grams zymin.
,, D = ,, ,, lævulose + ,, ,,
,, E = ,, 10 ,, dextrose + ,, ,,
,, F = ,, 5 ,, ,, + ,, ,, which has remained three hours at 30° with water.

Temp. 30°. Rate of fermentation in cm. per 10 mins.

t	*A.*	*B.*	*C.*	*D.*	*E.*	*F.*
0 minute	—	—	0·04	0·05	—	—
10 minutes	—	—	—	—	—	2·5
20 ,,	—	—	—	—	—	6·1 (*m*)
30 ,,	0·2	0·3	0·05	0·05	0·05	5·9
40 ,,	3·1 (*m*)	4·4 (*m*)	—	—	—	—
45 ,,	—	—	0·07	—	—	—
50 ,,	1·9	3·1	—	—	—	—
55 ,,	—	—	—	1·75	—	—
60 ,,	1·8	3·0	2·2	—	—	3·3
65 ,,	—	—	—	7·0	—	—
70 ,,	—	—	6·6	8·6 (*m*)	—	—
75 ,,	—	—	—	7·0	—	—
80 ,,	—	—	8·6 (*m*)	6·2	—	—
85 ,,	—	—	8·4	4·9	3·9	—
90 ,,	1·65	—	6·8	4·7	6·8 (*m*)	—
95 ,,	—	—	5·5	4·3	6·4	—
100 ,,	—	—	4·5	4·0	6·1	—
150 ,,	—	—	3·9	3·9	3·9	—
200 ,,	1·4	0·45	—	—	—	—
300 ,,	—	—	3·15	3·2	3·5	—
400 ,,	—	—	—	—	3·1	—
500 ,,	—	—	2·6	—	—	—

(*m*) = maximum velocity.

Solution G = 50 c.c. 5 per cent. dextrose + 2·5 grams "zymin."
,, H = ,, ,, ,, ,, ,, previously heated in water to a temperature of 95°.

t.	*G.*	*t.*	*H.*
100 minutes	0·0	55 minutes	0
150 ,,	0·5	70 ,,	2·2
184 ,,	1·3	80 ,,	2·5
200 ,,	2·1 (*m*)	85 ,,	3·0 (*m*)
210 ,,	1·8	90 ,,	2·7
225 ,,	1·45	95 ,,	2·7
240 ,,	1·2	100 ,,	2·5
300 ,,	1·0	200 ,,	2·0
500 ,,	0·9	400 ,,	2·0
		500 ,,	1·8

TABLE XVII.

The Influence of Potassium Phosphate on the Rate of Fermentation of Invert Sugar by Zymin and by Yeast.

Rate of fermentation of 5 per cent. invert sugar.

	5 grams zymin.	5 grams zymin + 5 c.c. phosphate solution.
Maximum	5·3 cm. per 10 mins.	8·8 cm. per 10 mins.
20 minutes later	3·0 ,, ,,	7·7 ,, ,,
60 ,, ,, ...	3·0 ,, ,,	4·4 ,, ,,

Brewery yeast + 50 c.c. 5 per cent. invert sugar	9·25 cm. per 6 mins.
,, + ,, + 0·1 c.c. phosphate solution	9·00 ,, ,,
,, + ,, + 1 c.c. ,, ,,	9·15 ,, ,,
,, + ,, + 3 c.c. ,, ,,	9·20 ,, ,,
,, + ,, + 5 c.c. ,, ,,	7·7 ,, ,,

TABLE XVIII.

Fermentation by Dried Yeast.

Solution A = 50 c.c. water + 5 grams dried yeast.
,, B = ,, ,, + ,, ,, + 5 c.c. phosphate solution.
,, C = ,, 5 per cent. dextrose + 2·5 grams dried yeast.
,, D = ,, ,, ,, ,, ,, + 5 c.c. phosphate solution.

	Rate of fermentation in cm. per 5 mins.			
t.	*A.*	*B.*	*C.*	*D.*
5 minutes	—	3·35	0·7	—
10 ,,	4·0	7·4 (*m*)	0·7	0·1
15 ,,	6·0 (*m*)	7·2	1·25	—
20 ,,	5·4	5·5	1·65	—
25 ,,	4·0	3·25	2·55	—
30 ,,	3·15	—	3·5	—
35 ,,	—	2·15	4·05 (*m*)	0·6
40 ,,	—	—	4·0	8·4
42½ ,,	—	—	—	14·8 (*m*)
45 ,,	2·05	1·35	—	14·0
50 ,,	—	—	3·4	—
55 ,,	1·3	—	3·05	9·2
60 ,,	—	—	—	7·8

The phosphate solution in all these experiments was made by dissolving 10 grams of Kahlbaum's dibasic potassium phosphate in 100 c.c. of $N/5$ sulphuric acid. It was neutral to litmus.

The Mechanism of Fermentation.

The results described in this communication show that many of the problems in connexion with fermentation are more easily investigated by the use of living yeast than by preparations from yeast, for fermentation is much less influenced by secondary reactions in the former case than when "Dauerhefe" or yeast juice is used to carry out the reaction.

Attempts have been made to bring into agreement the various results obtained by the measurements of the velocity of reaction. Those which are most important in determining the mechanism of fermentation may be summarised as follows:

1. The rate of fermentation of dextrose, lævulose, galactose, and mannose is approximately independent of the concentration of the sugar between the concentrations 1 gram to 10 grams per 100 c.c.

2. The fermentation of dextrose and lævulose under all conditions proceeds with approximately equal velocities.

3. The influence of temperature on the velocity of fermentation is approximately independent of the yeast used to bring about the reaction, and is almost the same in the case of the fermentation of dextrose, lævulose, and mannose, but the influence is somewhat less in the case of the reaction with galactose.

4. Many yeasts (very probably all yeasts) are unable to ferment galactose unless the yeast has been grown in the presence of this sugar. The ratio of the rate of fermentation of dextrose to that of galactose varies between very large limits. A variation of 100 : 0 to 100 : 155 has been observed with one race of yeast.

5. The ratio of the rate of fermentation of dextrose to mannose varies greatly, depending mainly on the treatment the yeast has undergone.

6. When two sugars are fermented simultaneously in the same solution, interference takes place between the reactions.

7. The velocity of fermentation by living yeast can easily be lessened by addition of certain inhibiting agents, but cannot be appreciably raised.

In whatever way the reaction is considered, we must first assume that the sugar diffuses into the yeast cell. There is no doubt that this reaction takes place so rapidly that it exercises no control on the velocity of evolution of carbon dioxide. The independence of the velocity with varying concentrations of sugar, the high temperature coefficient, and the fact that the fermentation starts immediately without any measurable induction period are practically conclusive on this point.

Velocity measurements give us information with regard to what is termed the controlling reaction. Fermentation is considered a series of successive reactions, and the controlling reaction is the one which proceeds slowest and has the largest influence on the velocity of formation of alcohol and carbon dioxide.

We may assume that this reaction is an enzyme reaction, and that the different sugars are fermented by the same or by different enzymes.

On the other hand, the assumption may be made that the controlling reaction is not an ordinary enzyme reaction, but some protoplasmic change which takes place in the cell.

An argument in favour of the last assumption is that fermentation by yeast juice is comparatively feeble, and sensitive to different reagents which take no direct part in the reaction. Fermentation by yeast cells is, however, much more constant. It would be very difficult on this assumption to account for the differences in the rate of fermentation of dextrose, galactose, and mannose, and to explain the rate of fermentation of mixed sugars. The results all point to an enzyme reaction involving in some way the sugar.

There is much to be said in favour of assuming that dextrose, galactose, and mannose are fermented by three different enzymes, which may conveniently be called glucozymase, galactozymase, and mannozymase. Glucozymase ferments dextrose and lævulose, galactozymase ferments galactose, and mannozymase ferments mannose. The different ratios of activity of yeast to dextrose, galactose, and mannose would admit of easy explanation by assuming that the enzymes were produced by some yeasts and not by others, and were sensitive in different degrees to heat and other influences. The main objections to this assumption are, firstly, all known yeasts which ferment any sugar ferment dextrose. Why should glucozymase be the first fermentation enzyme produced by the yeast? Again, the interference of two fermentation reactions when carried out simultaneously in the same solution has to be explained. We can get over the difficulty by assuming that mannose inhibits the fermentation of dextrose by glucozymase, and also that dextrose inhibits the fermentation of galactose by galactozymase. There is a certain amount of experimental evidence in favour of these suppositions.

If, on the other hand, we endeavour to work out the mechanism of fermentation on the assumption that one enzyme carries out the reaction with the four sugars, we get an explanation of the interference of the reactions by the competition for the enzyme when more than one fermentable sugar is present. To explain the varying ratios of the rates of fermentation of different sugars, we have to assume that the enzyme acquires different properties under different conditions.

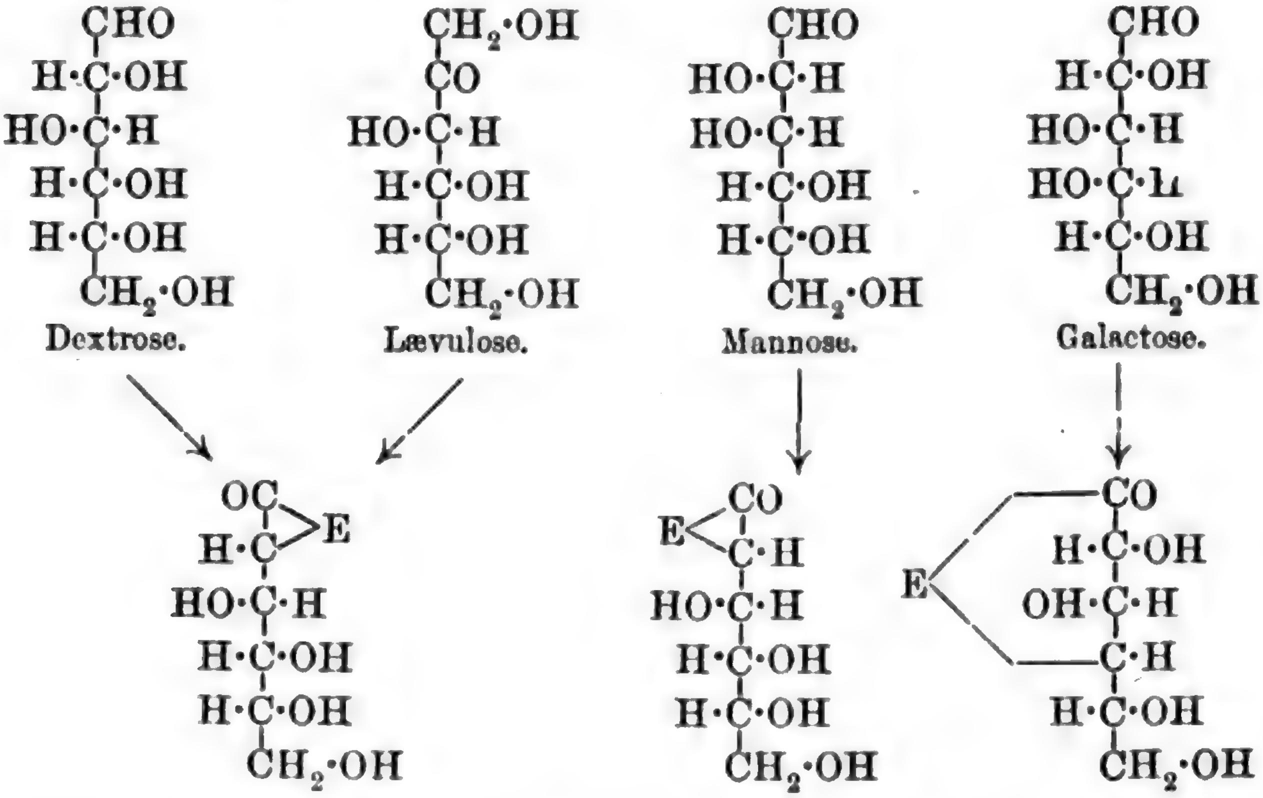
This is not altogether impossible. An analogy might be found in inorganic catalytic reactions if the investigation were carried out. Thus colloidal platinum has a catalytic influence on the decomposition of hydrogen peroxide (Bredig and Bernech, *Zeitsch. physikal. Chem.*, 1899, **31**, 258; Bredig and Ikeda, *ibid.*, 1901, **37**, 1), and also on the formation of water from hydrogen and oxygen dissolved in water (Ernst, *Zeitsch. physikal. Chem.*, 1901, **37**, 448). It is quite possible that the ratio of the activities of the platinum to the two reactions does not remain constant for different preparations and different treatments of the colloid. It is even possible that one might prepare a specimen of colloidal platinum which would catalytically influence one reaction without affecting the other. This would afford an exact analogy to the fermentation of dextrose and galactose by the enzyme in yeast.

In describing the measurements of fermentation of dextrose, lævulose, and invert sugar, it was pointed out that the results could be to a certain extent explained on the assumption that the sugar combines with the whole of the enzyme present, forming the same intermediate compound from either dextrose or lævulose. If we try to bring the results of the experiments on galactose and mannose into agreement, we have to assume a similar combination in these cases to account for the constant velocity with varying concentrations of sugar. The differences in the rates of fermentation of the different sugars can be explained on the assumption that different intermediate compounds are formed. It is not difficult to construct such compounds which will satisfy these conditions. We can assume that the compound is formed by simple addition of the enzyme and sugar, or by elimination of water according to the equations:

$$C_6H_{12}O_6 + E = C_6H_{12}O_6E$$

$$\text{or } C_6H_{12}O_6 + E = C_6H_{10}O_5E + H_2O.$$

The latter case is rather simpler, and the formulæ of the compounds may be constructed as follows:



In considering the possible formulæ in the case of galactose, that one has been chosen which agrees with the statement that *d*-tagatose and *d*-talose are not fermentable, although it is not known whether these sugars are fermented by yeast acclimatised to galactose.

The asymmetric character of the enzyme prevents the formation of many of the possible compounds isomeric with the above.

It is not suggested that these bodies are the only possible intermediate compounds, but rather that the mechanism of fermentation can be worked out on the assumption that the same enzyme ferments all four sugars, and that the different rates are determined by different intermediate compounds.

The supposition that more than one enzyme takes part in the fermentation of each sugar does not lead to any simpler explanation of the results.

The conclusions of this discussion may be summarised as follows:

The numerous results obtained by measurements of the velocity of the fermentation of dextrose, lævulose, mannose, and galactose are most easily brought into agreement on the supposition that the enzyme combines completely with the sugar, and that the velocity of formation of carbon dioxide is determined by the rate of decomposition of this compound. Dextrose and lævulose are fermented by the same enzyme, but the results are not considered conclusive in determining whether one enzyme brings about the fermentation of all four sugars.

The results also have some bearing on enzyme reactions in general. The main evidence generally recognised to distinguish two enzymes is a variation in the occurrence and relative activity of the two enzymes in question. Thus maltase is considered to be different from invertase in that yeasts are known which contain each enzyme singly, and that they are in different degrees sensitive to outside influences, such as heat. We can express the results in the manner used in this communication, that a variation in activity from 100:0 to 0:100 has been observed with different yeasts. If it is considered that a variation from 100:0 to 100:150 in activity of yeasts is not conclusive proof that dextrose and galactose are fermented by different enzymes, then the evidence to show that sucrose and maltose are hydrolysed by different enzymes ought to be reconsidered.

These two views can be expressed generally. On the one hand, we have the hypothesis that there is present in yeast cells a large number of enzymes each capable of exerting its own specific action; on the other, it is possible that only a few enzymes are present, and that the same enzyme can promote different chemical actions (compare H. E. Armstrong and E. F. Armstrong, *Proc. Roy. Soc.*, 1907, **79**, *B*, 360; Marino and Lericano, *Gazzetta*, 1907, **37**, i, 45). The first view is the more plausible one, and the one usually accepted, but, as there are differences between glucozymase, galactozymase, and mannozymase which are in some ways as great as the differences between the sucroclastic enzymes, this view also involves the assumption that these three fermentation enzymes are different.

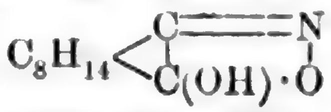
The author wishes to acknowledge his indebtedness to Dr. A. L. Stern, for valuable criticism of the work described in this paper.

BURTON-ON-TRENT.

XXII.—*Studies in the Camphane Series. Part XXV. Action of Diazomethane on the Two Modifications of* iso*Nitrosocamphor.*

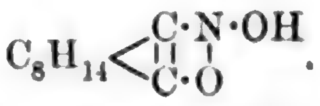
By MARTIN ONSLOW FORSTER and HENRY HOLMES.

APART from the general question of oxime structure and the advantages or drawbacks of the Hantzsch-Werner hypothesis, the constitution of *iso*nitrosocamphor presents features peculiar to itself. Although both modifications of this compound, melting at 152° (stable) and 114° (unstable) respectively, are produced by the original method of Claisen and Manasse (*Annalen*, 1893, **274**, 71), it does not appear to be possible to separate them by fractional crystallisation, and it was only by hydrolysing the isolated products of treating the mixture with *m*-nitrobenzoyl chloride that the unstable variety was revealed (Trans., 1903, **83**, 534). Since that time many experiments have been made with the object of explaining, from a chemical standpoint, the obscure relationship between the two compounds (Forster, Trans., 1904, **85**, 892; 1905, **87**, 232), but it cannot be claimed that the conclusions drawn therefrom achieve much more than bring the difficulties into stronger relief; moreover, these deductions have been disputed, although not, in our opinion, disproved, by the ingenious arguments of Baly, Marsden, and Stewart (Trans., 1906, **89**, 966), based on an examination of absorption spectra. Briefly stated, the conclusions of these authors amount to rejection of the stereochemical hypothesis, the isomerism of the two modifications of *iso*nitrosocamphor being regarded as structural:



$$C_8H_{14}\Big<\begin{array}{l}C=\!=\!=\!=N\\ |\qquad\quad\ \ |\\ C(OH)\cdot O\end{array}$$

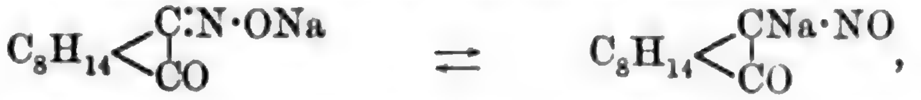
Stable (m. p. 152°).



$$C_8H_{14}\Big<\begin{array}{l}C\cdot N\cdot OH\\ \|\ \ \ |\\ C\cdot O\end{array}.$$

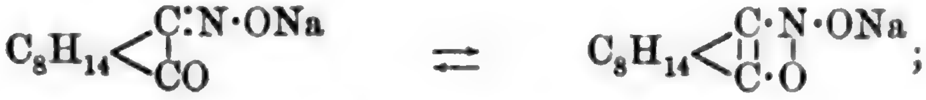
Unstable (m. p. 114°).

Whilst there is doubtless much to be said in favour of this representation of the stable variety, the case for the second formula appears to us very slender. It is based on the conclusion that the spectrometric data justify the recognition of an equilibrium mixture,



$$C_8H_{14}<\begin{array}{l}C{:}N\cdot ONa\\ |\\ CO\end{array} \quad \rightleftharpoons \quad C_8H_{14}<\begin{array}{l}CNa\cdot NO\\ |\\ CO\end{array},$$

in the alkaline solution of unstable *iso*nitrosocamphor, giving rise to isorropesis expressed by



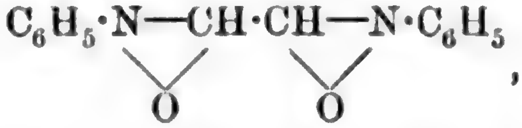
$$C_8H_{14}<\begin{array}{l}C{:}N\cdot ONa\\ |\\ CO\end{array} \quad \rightleftharpoons \quad C_8H_{14}<\begin{array}{l}C\cdot N\cdot ONa\\ \|\quad |\\ C\cdot O\end{array};$$

but it does not appear why, in selecting from these two an expression for the parent compound, the latter, instead of the former, should have been chosen. Moreover, the conclusion is based on a line of argument which, we venture to think, has at least one serious weakness. The absorption spectrum of the unstable isomeride was never studied individually, it was merely deduced from the difference between the curves furnished by the "Claisen mixture" and by the stable modification, this difference being ascribed to the unstable form. Such a course might be justified if it were perfectly certain that the "Claisen mixture" is nothing more than a simple mixture of the two modifications, but one of the difficulties of the problem lies in the peculiarity that, although an artificial mixture of the two substances yields the unstable variety by fractional crystallisation, separation cannot be effected when the "Claisen mixture" itself is treated in the same way.

It was not our intention to complicate the matter still further by re-opening the discussion, but a new fact has arisen from an attempt to gain fresh evidence by studying the behaviour of the two isomerides towards diazomethane. We find that this agent rapidly transforms the unstable variety into the stable form, whilst the latter is converted into the *N*-methyl ether, and as a consequence of this observation it will be necessary to proceed very cautiously in drawing conclusions regarding the structure of a compound from its behaviour towards diazomethane. We have searched in vain for records of the interaction of diazomethane and oximes, in the hope of being able to make, from our own experiments, some inference regarding the constitution of *iso*nitrosocamphor; a preliminary examination of the benzaldoximes has shown us that the *anti*-aldoxime (m. p. 35°) yields the *O*-methyl ether, whilst the *syn*-aldoxime (m. p. 128°) remains unaltered. The benziloximes have furnished oily products from which no definite conclusion can be drawn.

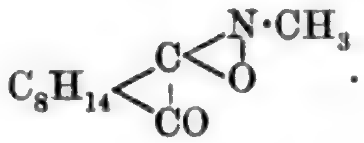
Nevertheless, experiments have been described by other workers which bear indirectly upon the problem, in view of the conclusion by

Baly, Stewart, and Marsden regarding the possible presence of a nitroso-group. It has been shown by von Pechmann (*Ber.*, 1897, **30**, 2461) that nitrosobenzene yields with diazomethane the glyoxime *N*-phenyl ether,



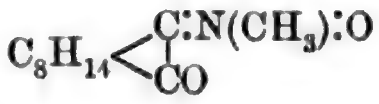
$$C_6H_5\cdot N\!-\!CH\cdot CH\!-\!N\cdot C_6H_5 \quad (\text{each } N\text{–}CH \text{ bridged by } O),$$

subsequent experiments (von Pechmann and Nold, *Ber.*, 1898, **31**, 557) indicating that the formation of a glyoxime *N*-phenyl ether is the normal result of action between an aromatic nitroso-compound and diazomethane. At first sight, this might be regarded as disposing finally of the possible presence of a nitroso-group in *iso*nitrosocamphor, because, apart from the formation of an ethane derivative as distinguished from the simple methane compound, doubtless due to the oxidising action of nitrosobenzene, the condition of the phenyl group with respect to oxygen is quite distinct from that of the camphoryl radicle in the *N*-methyl ether of *iso*nitrosocamphor as represented by the formula:



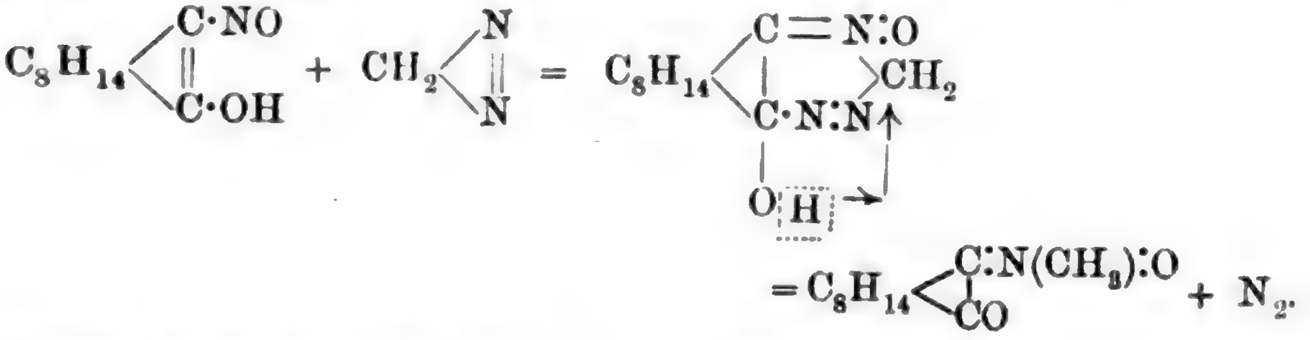
$$C_8H_{14}<\begin{matrix} C<\begin{matrix} N\cdot CH_3 \\ | \\ O \end{matrix} \\ | \\ CO \end{matrix}.$$

But analogy may be pressed too far, and it is impossible to deny that the behaviour of the stable *iso*nitrosocamphor towards diazomethane may be construed as readily in favour of a nitroso-group, according to the view which is taken concerning the structure of the *N*-methyl ether. This compound, obtained in association with the *O*-ether by the action of methyl iodide on *iso*nitrosocamphor in presence of sodium methoxide (Trans., 1904, **85**, 896), is pale yellow, has high specific rotatory power, and is resolved by acids into camphorquinone and alkylhydroxylamine with extraordinary facility, points in which it is closely resembled by the ethyl compound described in this communication; accordingly, we are disposed to prefer the representation

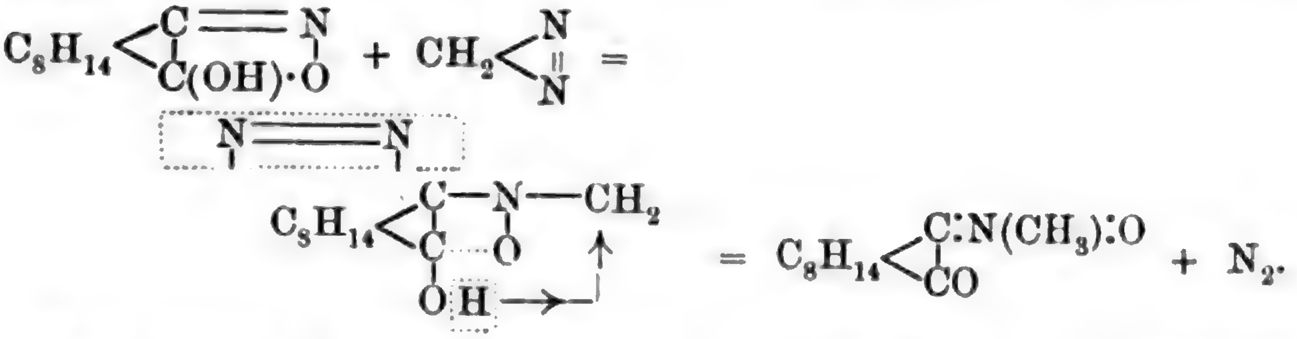


$$C_8H_{14}<\begin{matrix} C{:}N(CH_3){:}O \\ | \\ CO \end{matrix}$$

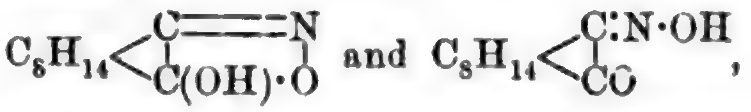
to the one already given, and Mr. Baly informs us that his examination of the absorption spectrum has led him, independently, to the same conclusion. There seems to be little doubt that the various changes which diazomethane has been shown to effect can be explained on the assumption that the complex $-N{:}N\cdot CH_2-$ is assimilated by some unsatisfied affinity of the co-operating molecule, the product then losing nitrogen in some cases, and retaining it in others. If now a nitroso-group were present in the camphor derivative, the production of the *N*-methyl ether would be met by the following explanation :



Nevertheless, we cannot admit that *iso*nitrosocamphor is a true nitroso-compound. The absence of a green or blue coloration on dissolution and fusion, together with the failure of the Liebermann test, must not be set aside without the strongest evidence. Moreover, the action of diazomethane can be explained by adopting the formula which is certainly indicated from the behaviour of the colourless methyl and benzoyl derivatives :



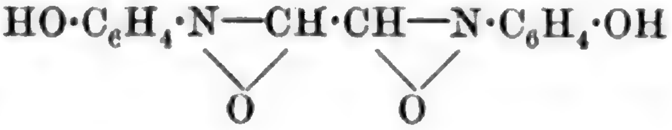
We have not recognised the colourless methyl ether as accompanying the *N*-ether when diazomethane acts on the stable modification of *iso*-nitrosocamphor, but its absence does not bear materially on the relative merits of the formulæ :



$$C_8H_{14}<\begin{array}{l}C{=\!=}N\\C(OH)\cdot O\end{array} \text{ and } C_8H_{14}<\begin{array}{l}C{:}N\cdot OH\\CO\end{array},$$

because the formation of quinonemonoxime *O*-methyl ether in association with the dihydroxy-derivative of glyoxime *N*-phenyl ether,

$O{:}C_6H_4{:}N\cdot O\cdot CH_3$ and

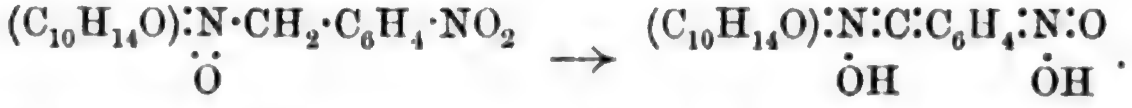


$$HO\cdot C_6H_4\cdot N\!-\!CH\cdot CH\!-\!N\cdot C_6H_4\cdot OH$$

when diazomethane acts on nitrosophenol (von Pechmann and Seel, *Ber.*, 1898, **31**, 296) may be merely due to the more acidic character of the hydroxyl group in the latter substance, and the existence of a hydroxyl radicle in *iso*nitrosocamphor is not disputed.

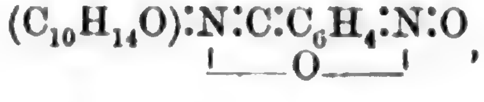
The action of diazomethane on oximino-compounds in general will probably develop into a fruitful subject for inquiry. It is particularly significant that the β-benzaldoxime escapes attack under conditions which transform the isomeride into the *O*-methyl ether. This observation is probably as damaging to the stereochemical hypothesis as any which has been made, and is in agreement with experiments recently described in connexion with oxime isomerism by Beck and Hase (*Annalen*, 1907, **355**, 29), who have been led to conclude that the benzaldoximes are structurally distinct.

In conjunction with the foregoing subject, we have studied the action of *p*-nitrobenzyl chloride on *iso*nitrosocamphor in presence of sodium ethoxide, and have obtained three compounds, the relationship of which is not easy to explain. The principal crystalline product, melting at 175°, has the composition of a *p*-nitrobenzyl ether of *iso*nitrosocamphor, $C_{17}H_{20}O_4N_2$, but associated therewith, and occurring in small quantities only, is a substance having the appearance of iodoform and melting at 214°, with an empirical formula $C_{17}H_{18}O_3N_2$. It is difficult to understand the change giving rise to the latter compound, because we have not been able to prepare it by another method, but it may depend on the fact that a large proportion of the material employed is converted into a pale red, viscous oil, which develops an intense blue coloration with alcoholic potash. The scarcity of chromophoric substances in the camphor group renders this product a remarkable one, but, unfortunately, all attempts to prepare crystalline derivatives of the oil have failed. The only explanation of the colour which has hitherto suggested itself, depends on the possibility that the oil may be the *N*-*p*-nitrobenzyl ether of *iso*nitrosocamphor, which, if represented by the type of expression advanced in the present communication, might be expected to change into a dienolic form with alkalis:



$$(C_{10}H_{14}O){:}\underset{\overset{\cdot\cdot}{O}}{N}\cdot CH_2\cdot C_6H_4\cdot NO_2 \longrightarrow (C_{10}H_{14}O){:}\underset{\overset{\cdot}{O}H}{N}{:}C{:}C_6H_4{:}\underset{\overset{\cdot}{O}H}{N}{:}O .$$

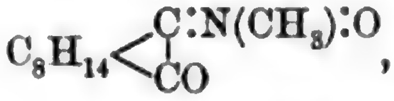
The bright yellow compound, melting at 214°, is conceivably the anhydride of this dienol,



$$(C_{10}H_{14}O){:}N{:}\underbrace{C{:}C_6H_4{:}N}_{O}{:}O ,$$

as the dissolved substance is rapidly decomposed by light, and decolorises bromine immediately. The interaction of *iso*nitrosocamphor and *p*-nitrobenzyl chloride is rendered still more obscure by the fact that *p*-nitrobenzyl bromide, acting in presence of silver oxide, yields an isomeric substance of composition $C_{17}H_{20}O_4N_2$, melting at 114°, together with the colour-giving oil.

Although the foregoing remarks on the nature of these products are purely speculative, it has appeared desirable to record our experiments because another remarkable chromophoric substance is produced when iminocamphor is led to combine with formaldehyde, the product developing an intense magenta-red coloration with alcoholic potash. It seemed to us possible that if the *N*-methyl ether has the constitution



$$C_8H_{14}<\begin{matrix}C:N(CH_3):O \\ | \\ CO\end{matrix},$$

such a substance, with empirical formula $C_{11}H_{17}O_2N$, might arise from iminocamphor and formaldehyde:

$$C_{10}H_{15}ON + CH_2O = C_{11}H_{17}O_2N.$$

From this point of view, the experiment failed. Iminocamphor and formaldehyde certainly combine under the influence of acids in minute quantity, but the product is not the *N*-methyl ether; the intensely chromophoric material actually obtained has been isolated for a few minutes in the form of a sodium derivative which resembles indigo-blue in appearance, but this is immediately destroyed by acids, yielding camphorquinone, ammonia, and formaldehyde.

EXPERIMENTAL.

Action of Diazomethane on iso*Nitrosocamphor.*

One gram of *iso*nitrosocamphor (stable modification, m. p. 152°), dissolved in pure dry ether, was treated with an ethereal solution of diazomethane prepared from 2·5 c.c. of nitrosomethylurethane; as the agent was added, the yellow colour of the earlier portions disappeared immediately, and vigorous evolution of gas took place. After twenty-four hours, the liquid was extracted with very dilute aqueous potash, in which a faint coloration was developed, and on evaporating the ether there remained a yellow oil, readily identified as the *N*-methyl ether of *iso*nitrosocamphor.

On treating the unstable modification (m. p. 114°) with diazomethane under similar conditions, involving excess of the agent, the same product arose, but the following experiment indicates that the formation of the *N*-methyl ether is preceded by conversion of the unstable *iso*nitrosocamphor into the isomeric substance. Two equal portions of the unstable form were dissolved in ether, and, the solutions being of similar concentration, one was treated with a small quantity of diazomethane, representing a considerable deficit from one molecular proportion; after six hours in stoppered vessels, both solutions were allowed to evaporate spontaneously, the residue in each case being recrystallised from hot petroleum (b. p. 60—80°). From the blank experiment, the original material (m. p. 114°) was recovered, whilst the specimen which had been treated with a deficiency of diazomethane, furnished the stable modification (m. p. 152°) contaminated with a very small proportion of the *N*-methyl ether. These experiments have been repeated several times.

by Google

Interaction of p-Nitrobenzyl Chloride and iso*Nitrosocamphor in Presence of Sodium Ethoxide.*

Fifty grams of *iso*nitrosocamphor were covered with 400 c.c. of absolute alcohol in which 6·5 grams of sodium had been dissolved; 47 grams of finely-powdered *p*-nitrobenzyl chloride suspended in 100 c.c. of alcohol were added to the dark red solution, this colour changing through green to dark blue as the mixture was heated on the water-bath. When boiled, however, the dark blue liquid suddenly became pale brown, and a precipitate appeared, augmenting during two to three hours; heating was discontinued, and after an interval of twelve hours the pale brown, crystalline deposit was filtered, the filtrate being evaporated to small bulk, and diluted with water. A further quantity of crystals separated, differing in appearance from the first crop; the remaining product was a viscous, red oil.

The Compound, $C_{17}H_{20}O_4N_2$.—The less soluble material referred to above weighed 25 grams, and when twice recrystallised from boiling alcohol yielded lustrous, transparent, pale brown prisms, melting at 175° without evolving gas:

0·1839 gave 0·4343 CO_2 and 0·1001 H_2O. C = 64·40; H = 6·10.
0·3112 ,, 24·2 c.c. of nitrogen at 19° and 756 mm. N = 8·89.
$C_{17}H_{20}O_4N_2$ requires C = 64·55; H = 6·33; N = 8·86 per cent.

A solution containing 0·2694 gram in 25 c.c. of chloroform gave α_D 2°39′ in a 2-dcm. tube, whence $[\alpha]_D$ 123·0°, this value remaining unchanged after four weeks' exposure to light. Attempts to obtain an oxime from this compound, or definite products of hydrolysis with acids and alkalis in alcoholic solution, have been unsuccessful. When heated at the melting point during a few minutes, the fused substance becomes pasty, owing to the separation of *p*-dinitrostilbene, which melts at 280—285°.

The Compound, $C_{17}H_{18}O_3N_2$.—The second crop of crystals amounted to about 2 grams only, and, in ten or more experiments which have been made since, occurred in even smaller quantity, or not at all. After treatment with a little cold alcohol to remove the oily mother liquor, the substance was crystallised from the hot solvent, separating in lustrous, transparent, canary-yellow plates, melting at 214° without evolving gas:

0·1821 gave 0·4544 CO_2 and 0·1043 H_2O. C = 68·06; H = 6·42.
0·2640 ,, 22·2 c.c. of nitrogen at 18° and 761 mm. N = 9·72.
$C_{17}H_{18}O_3N_2$ requires C = 68·45; H = 6·04; N = 9·40 per cent.

A solution containing 0·5737 gram in 25 c.c. of chloroform, when freshly prepared, gave α_D $-3°0'$ in a 2-dcm. tube, corresponding with $[\alpha]_D$ $-65·3°$, but this rotation diminished when the liquid was exposed to diffused daylight, reaching $[\alpha]_D$ −55·5° in about three hours; on further exposure, the solution became deep brown, with green fluorescence, and was too dark to examine in the polarimeter.

The substance is insoluble in cold petroleum, but dissolves in the boiling liquid, forming a colourless solution which deposits the characteristic yellow plates on cooling.

The Chromophoric Oil.—The viscous, red oil remaining after the compounds, $C_{17}H_{20}O_4N_2$ and $C_{17}H_{18}O_3N_2$, have been removed, represents the main bulk of the product from *iso*nitrosocamphor and *p*-nitrobenzyl chloride. The oil is insoluble in water, but dissolves readily in organic media, and on adding caustic alkali to its solutions in methyl, ethyl, or *iso*butyl alcohol an intense blue coloration is developed; this change does not take place, however, when ether, benzene, chloroform, petroleum, or phenol is used as a medium in place of the alcohols, but the colour is developed by baryta as strongly as by potash or soda, and more slightly by alcoholic ammonia. The blue solution loses its colour on adding excess of the oil which produces it, and dilution with water has the same effect; acids also destroy the colour, which is restored by alkalis.

Attempts to convert this compound into a permanent, crystalline derivative which could be analysed have been unsuccessful; it is not volatile in steam, and an attempt to distil under 2 mm. pressure led to complete decomposition at 140—150°, neither the distillate nor the residue giving the faintest indication of the blue colour after this treatment, although continued exposure to 100° has no effect on the chromophoric properties. Nevertheless, the colour-giving oil appears to be the uniform companion of the *p*-nitrobenzyl derivative of *iso*nitrosocamphor as prepared above, and we have obtained it also when sodium dissolved in *iso*butyl alcohol is substituted for sodium ethoxide, although under these conditions the crystalline derivatives do not appear. Moreover, a paste composed of the potassium derivative of *iso*nitrosocamphor, *p*-nitrobenzyl chloride, and alcohol, remaining at the laboratory temperature during many days, develops the chromophoric substance together with the compound $C_{17}H_{20}O_4N_2$.

In view of the fact that, associated with the foregoing products, there is produced in varying proportion the *p*-dinitrostilbene, melting at 280—285°, obtained by Walden and Kernbaum (*Ber.*, 1890, **23**, 1959) from *p*-nitrobenzyl chloride and alcoholic potash, it seemed possible that the chromophoric substance was a stilbene derivative; the authors quoted, however, do not refer to a compound of this nature, and on repeating their experiment we failed to recognise the oil furnished by the camphor derivative. Moreover, the compound is not produced when *iso*nitrosocamphor is heated with benzyl chloride in presence of sodium ethoxide.

Interaction of p-*Nitrobenzyl Bromide and* iso*Nitrosocamphor in Presence of Silver Oxide.*

When *p*-nitrobenzyl bromide acts on *iso*nitrosocamphor in presence of sodium ethoxide, the blue coloration is developed as in the case of the chloride, and quickly disappears on warming, but the compounds, $C_{17}H_{20}O_4N_2$ and $C_{17}H_{18}O_3N_2$, do not appear to be formed, the sole products being *p*-dinitrostilbene and the colour-giving oil. On repeating the experiment with dry silver oxide instead of sodium ethoxide, silver bromide quickly separated, and the filtered liquid deposited colourless prisms which melted at 114°:

0·2055 gave 0·4871 CO_2 and 0·1207 H_2O. C = 64·63; H = 6·58.
0·3154 „ 23·9 c.c. of nitrogen at 16° and 765 mm. N = 8·98.
$C_{17}H_{20}O_4N_2$ requires C = 64·55; H = 6·33; N = 8·86 per cent.

A solution containing 0·3502 gram in 25 c.c. of chloroform gave a_D 3°52′ in a 2-dcm. tube, whence $[a]_D$ 138·0°.

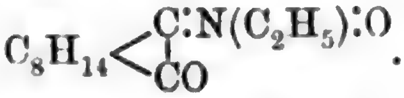
This compound does not arise when *p*-nitrobenzyl chloride is used instead of the bromide, the sole recognisable product being the colour-giving oil, which also accompanies the crystalline compound in the foregoing experiment. As in the case of the pale brown isomeride melting at 175°, attempts to obtain an oxime, or definite products of hydrolysis, have failed, and accordingly the relationship between the two isomerides remains unexplained.

Action of Formaldehyde on Iminocamphor.

One gram of camphorylazoimide was converted into iminocamphor by suspending the ethereal solution over 2 c.c. of 40 per cent. aqueous potash, and adding 2 drops of absolute alcohol; when effervescence ceased, the ether was filtered, cooled in melting ice, and mixed with an ethereal solution of formaldehyde. One drop of 10 per cent. sulphuric acid was added, and the liquid, still at 0°, stirred during fifteen minutes. On adding sodium methoxide dissolved in methyl alcohol, an intense, magenta-red coloration was developed, and ether precipitated a bulky, amorphous solid; the filtered product, when drained on earthenware, consisted of an indigo-blue substance with bronze lustre, but was too unstable to admit of complete examination, quickly disappearing from the tile. The freshly-prepared substance, however, displayed properties which might be expected in the sodium derivative of a highly unstable compound from iminocamphor and formaldehyde. On covering the solid with cold dilute sulphuric acid, the colour was destroyed immediately, and effervescence took place; the odour of formaldehyde was noticeable, and became very intense on boiling, when camphorquinone separated. After the latter had been removed by extracting the cold liquid with ether, ammonium sulphate remained in the solution, but hydroxylamine was absent.

An ethereal solution of the substance gives no distinctive indication with ferric chloride or copper acetate, and, although attempts have been made to isolate some crystallisable derivative, neither benzoyl chloride nor the *m*-nitro-derivative has furnished a stable product. The colour change does not occur when camphorylazoimide itself is treated in the same way, nor will iminocamphor yield a compound with formaldehyde unless the mixture is treated with a small quantity of acid. It is possible, however, to substitute acetic for sulphuric acid, and the former agent has the advantage of hydrolysing the imine less freely than mineral acid; on the other hand, the colour produced by alcoholic alkali is less intense when acetic acid has been employed. If the magenta solution is diluted with water, the colour disappears after a few minutes have elapsed, and is not restored by potash; nevertheless, on adding enough acid, mineral or acetic, to destroy the red colour of an undiluted solution, alkali develops it once more.

The N-*Ethyl Ether of* iso*Nitrosocamphor*,



$$C_8H_{14}<\begin{matrix}C{:}N(C_2H_5){:}O \\ | \\ CO\end{matrix}.$$

One hundred grams of *iso*nitrosocamphor were mixed with 500 c.c. of absolute alcohol in which 13 grams of sodium had been dissolved, and heated on the water-bath with 95 grams of ethyl iodide under reflux during two hours. Alcohol and unused iodide having been removed by distillation, a current of steam was passed through the liquid in order to separate the *O*-ethyl ether, a colourless solid which melts at 73°, and is volatile in steam; on adding sodium carbonate to the filtered liquid, the *N*-ethyl ether was precipitated, and, after drying the ethereal extract with calcium chloride, was deposited on evaporation in the form of pale yellow crystals melting at 57°:

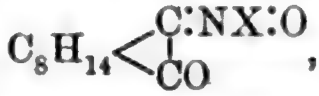
0·2447 gave 14·7 c.c. of nitrogen at 17° and 756 mm. N = 6·66.

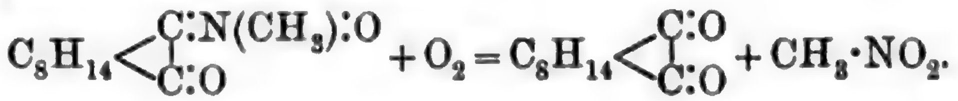
$C_{12}H_{19}O_2N$ requires N = 6·69 per cent.

A solution containing 0·3116 gram in 25 c.c. of chloroform gave α_D 6°11′ in a 2-dcm. tube, whence $[\alpha]_D$ 248·1°.

The *N*-ethyl ether is less soluble in hot water than in cold, which dissolves it readily, and from which it is precipitated by sodium carbonate or caustic potash; it is freely soluble in organic media. When heated with Fehling's solution, the latter is reduced, and boiling dilute acids resolve it immediately into camphorquinone and ethylhydroxylamine.

Action of Hydrogen Peroxide on Camphorquinone.

With the object of confirming the evidence in favour of the general formula,  $C_8H_{14}<\genfrac{}{}{0pt}{}{C{:}NX{:}O}{CO}$, for the *N*-alkyl ethers of *iso*nitrosocamphor, an attempt was made to oxidise the first member of the series with hydrogen peroxide in the hope that this agent would convert it into camphorquinone and nitromethane:



$$C_8H_{14}<\genfrac{}{}{0pt}{}{C{:}N(CH_3){:}O}{C{:}O} + O_2 = C_8H_{14}<\genfrac{}{}{0pt}{}{C{:}O}{C{:}O} + CH_3{\cdot}NO_2.$$

An aqueous solution of the *N*-methyl ether was therefore heated on the water-bath with hydrogen peroxide, when a colourless, viscous oil separated, and did not re-dissolve on cooling; although some change is thereby indicated, nitromethane could not be recognised. On heating the product with dilute sulphuric acid, a faint yellow colour was developed, and the liquid deposited a colourless solid on cooling; recrystallisation from water, followed by analysis, showed this to be camphoric anhydride:

0·1771 gave 0·4268 CO_2 and 0·1236 H_2O. C = 65·73; H = 7·75.

$C_{10}H_{14}O_3$ requires C = 65·96; H = 7·69 per cent.

Suspecting that the anhydride might arise also from camphorquinone, 10 grams of the latter were mixed with 50 c.c. of 30 per cent. hydrogen peroxide, when the paste became hot and inflated with gas; after thirty-six hours, the colour of the quinone had disappeared, and the product was readily identified with camphoric anhydride.

ROYAL COLLEGE OF SCIENCE, LONDON,
SOUTH KENSINGTON, S.W.

XXIII.—*The Constitution of Umbellulone. Part III.*

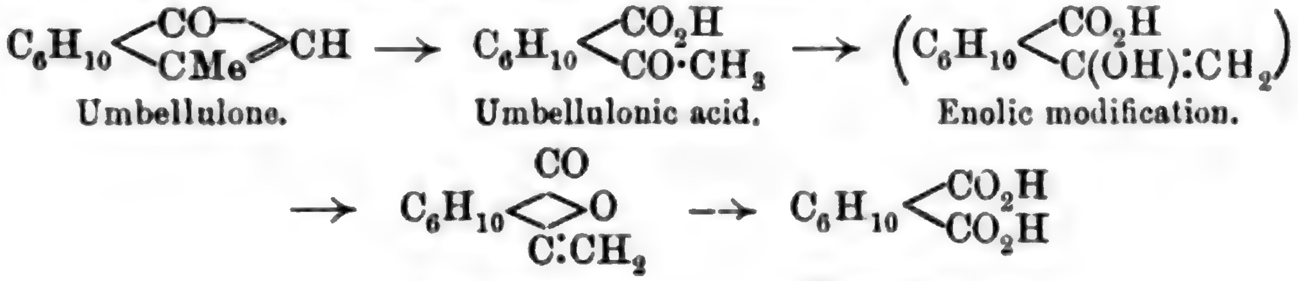
By FRANK TUTIN.

IN previous communications (Trans., 1906, **89**, 1104; 1907, **91**, 271) the author's conclusions respecting the constitution of umbellulone have been set forth, but in view of some criticisms recently published by Semmler (*Ber.*, 1907, **40**, 5017) it appears desirable that the subject should again be discussed.

Umbellulone was first isolated by Power and Lees (Trans., 1904, **85**, 629) from the essential oil of *Umbellularia Californica*, Nuttall

(Californian laurel). It was shown by them to possess the formula $C_{10}H_{14}O$, and to be a bicyclic ketone containing an ethylenic linking in the $\alpha\beta$-position with respect to the carbonyl group.

In the first communication by the present author, the behaviour of umbellulone on oxidation with potassium permanganate was studied. When submitted to this treatment, it gave a saturated keto-acid, umbellulonic acid, $C_9H_{14}O_3$, which on distillation passes into an unsaturated lactone, $C_9H_{12}O_2$. The latter, on oxidation, yielded umbellularic acid, a polymethylenedicarboxylic acid, possessing the formula $C_8H_{12}O_4$. These changes may be represented as follows:



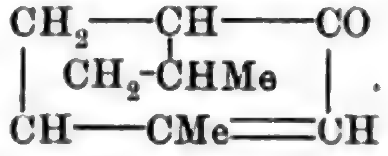
$$C_6H_{10}<\begin{matrix}CO-\\CMe=\end{matrix}>CH \rightarrow C_6H_{10}<\begin{matrix}CO_2H\\CO\cdot CH_3\end{matrix} \rightarrow \left(C_6H_{10}<\begin{matrix}CO_2H\\C(OH){:}CH_2\end{matrix}\right)$$

Umbellulone. Umbellulonic acid. Enolic modification.

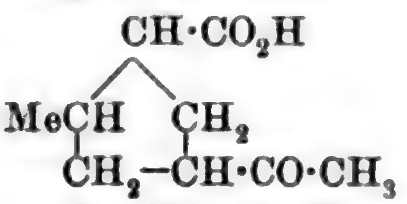
$$\rightarrow C_6H_{10}<\begin{matrix}CO\\C{:}CH_2\end{matrix}>O \rightarrow C_6H_{10}<\begin{matrix}CO_2H\\CO_2H\end{matrix}$$

Lactone. Umbellularic acid.

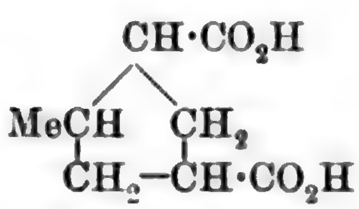
It was stated regarding umbellularic acid, that its general properties, especially its great stability, "indicate that it is one of the tetra-, penta-, or hexa-methylenedicarboxylic acids." It was not, however, at that time considered necessary to state in detail the reasons for concluding that it could not be a trimethylene compound. Since the hexamethylenedicarboxylic acids are all known, and the oxidation products of umbellulone are not identical or stereoisomeric with those of pinene, it was concluded that umbellularic acid was most probably a methylpentamethylenedicarboxylic acid. From these results, together with other considerations (*loc. cit.*), it was concluded that umbellulone was most probably represented by the following formula:



Umbellulonic and umbellularic acids respectively, would then have the following constitutions:



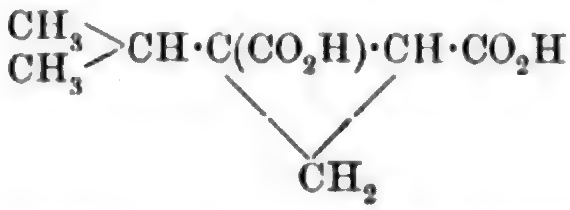
Umbellulonic acid.



Umbellularic acid.

This conclusion is in harmony with the observation, recorded in the author's second paper (*loc. cit.*), that when the ring contained in umbellulonic acid is opened by the addition of two atoms of hydrogen, δ-hydroxy-α-*iso*propyl-n-hexoic acid is obtained.

Although, as stated above, the reasons for concluding that umbellularic acid was not a trimethylene compound were not detailed in the original communication, it now appears necessary that these should be considered. If umbellularic acid does not contain a five-membered ring, it must be represented by the following formula:



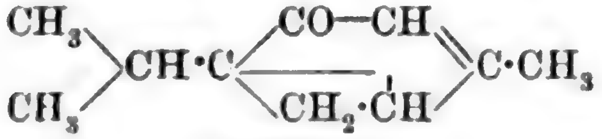
It is well known, however, that the *cyclo*propane ring is, in general, somewhat unstable. A. Kötz has pointed out (*J. pr. Chem.*, 1903, [ii], 68, 174) the generalisation that simultaneous substitution by a carboxyl group and an alkyl or phenyl radicle decreases the stability of the *cyclo*propane ring, and, furthermore, that in the presence of an alkyl or phenyl group the instability increases with the number of carboxyl groups. With consideration of these conclusions, O. Aschan (*Chemie d. Alicyclischen Verb.*, 1905, p. 244) adds that, in general, the occurrence of a quaternary carbon atom appears to increase the readiness with which the *cyclo*propane ring is opened. According to these generalisations, the *iso*propyl*cyclo*propanedicarboxylic acid represented above should be a compound in which the ring is readily ruptured, for it contains a *cyclo*propane ring substituted with an alkyl radicle and two carboxyl groups, and, moreover, it also contains a quaternary carbon atom.

Umbellularic acid, however, is an extremely stable substance. It is unaltered by heating with concentrated hydrochloric acid for five hours at 190°, and hydrobromic acid also has no action on it. It is not appreciably oxidised by alkaline potassium permanganate at 60°, and was recovered unchanged after boiling for ten hours with eight times its weight of a mixture of three parts of fuming nitric acid and one part of water. When heated for two hours on the water-bath with bromine and red phosphorus, it was also recovered unchanged, and after boiling for five hours with undiluted fuming nitric acid, besides unchanged umbellularic acid, only a trace of oxalic acid was obtained. In addition to considerations concerning the stability of the ring, it would not be expected that a compound containing an *iso*propyl group would exhibit such great stability towards nitric acid, as *p*-cymene, for example, when treated with this acid in the cold, gives *p*-tolyl methyl ketone, together with other compounds, and when warmed with nitric acid yields *p*-toluic acid. *iso*Propylsuccinic acid, also, is fairly readily attacked when heated with fuming nitric acid. The properties of umbellularic acid therefore certainly seem to indicate that it does not possess the *cyclo*propane structure.

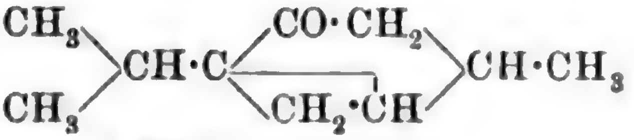
Semmler, in his recent publication (*loc. cit.*), states in the first place that the physical properties of umbellulone are not in agreement with those of *bicyclo*-2 : 2 : 2-octanone (*Ber.*, 1907, **40**, 4844), and that therefore either umbellulone or the *bicyclo*-2 : 2 : 2-octanone must be incorrectly represented.

In this connexion it may be noted first of all that Semmler has evidently never had even approximately pure umbellulone in his possession. Furthermore, if umbellulone is represented by the formula which I have proposed, it is not analogous to Semmler's octanone, since the latter, having the bridge in the para-position, can be represented only as a *cyclo*hexane compound with a bridge of two carbon atoms, whilst the former contains a meta-bridge, and can, with equal correctness, be represented as a *cyclo*hexane compound with a bridge of two carbon atoms, or as a *cyclo*heptane derivative with a bridge of one carbon atom. Lastly, experimental proof of the correctness of the formula assigned by Semmler to his "*bicyclo*-2 : 2 : 2-octanone" appears to be lacking.

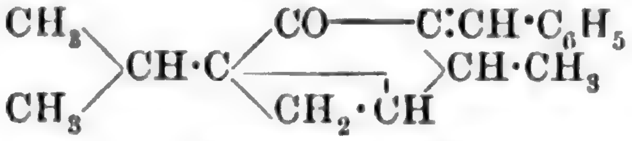
Semmler then proceeds to prepare the material which I had designated "β-dihydroumbellulone," from which he forms a hydroxymethylene and a benzylidene derivative, and, by oxidation of the latter, obtains *d*-homotanacetonedicarboxylic acid. This series of changes he represents as follows:



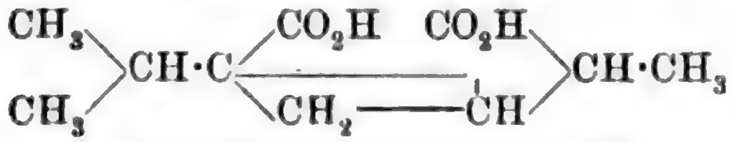
Umbellulone.



β-Dihydroumbellulone.



Benzylidene derivative.



Homotanacetonedicarboxylic acid.

From these results, Semmler is led to the conclusion that umbellulone is an unsaturated "tanacetone of the menthone series," in which the double linking is adjacent to the ketonic group. Umbellularic acid would consequently be 1-*iso*propyl*cyclo*propane-1 : 2-dicarboxylic acid, but, as I have pointed out above, its properties are not in accordance with this view.

With the exception of Semmler's remark concerning the physical properties of umbellulone, which has already been dealt with, his conclusions regarding the constitution of this ketone are based entirely on experiments conducted with "β-dihydroumbellulone" and its derivatives. It is of paramount importance therefore to inquire into the nature of the preparation which, in my first paper on umbellulone, I had designated as "β-dihydroumbellulone." In the first place, however, consideration may be given to the character of the "umbellulone" employed by Semmler.

The material available to Semmler for the purpose of his investigation of umbellulone consisted of 100 grams of the essential oil of *Umbellularia Californica* which had been supplied to him, at his request, by Dr. Power. This oil was a portion of the identical material which had been used in my work on umbellulone. It is stated by Semmler that the umbellulone can be separated from this oil by fractional distillation, but this is not strictly correct, as by this means it is impossible to obtain the pure ketone. Power and Lees (*loc. cit.*), by a very careful and prolonged fractionation of 1200 grams of the oil, obtained a fraction boiling at 217—222° (a_D - 36°33′ in a 1-dcm. tube) which gave, on analysis, C = 78·9; H = 9·9. On subjecting this to further fractionation, a portion was obtained which boiled constantly at 218°, and, on analysis, gave C = 79·1; H = 9·8. Since $C_{10}H_{14}O$ requires C = 80·0; H = 9·3, and $C_{10}H_{16}O$ requires C = 78·9; H = 10·5, these fractions were evidently mixtures. Moreover, on treating the fraction, b. p. 217—222°, with semicarbazide, it gave, at the most, only 55 per cent. of the theoretical yield of semicarbazidodihydroumbellulonesemicarbazone. That this deficiency is not due solely to the incomplete interaction of the ketone and the base, is seen from the fact that a very much better yield of the semicarbazido-derivative may be obtained by employing pure, regenerated umbellulone. Umbellulone, when regenerated from its semicarbazidosemicarbazone, has a_D - 37° in a 1-dcm. tube, and gave C = 79·7; H = 9·3 ($C_{10}H_{14}O$ requires C = 80·0; H = 9·3 per cent.). Since the product which Semmler regarded as umbellulone had a_D - 31°30′ in a 1-dcm. tube, it was evidently still more impure than the fraction (b. p. 217—222°, a_D - 36° 33′) obtained by Power and Lees, which, as shown above, and as recognised by them, was a mixture of substances.

It was therefore with consideration of the uncertainty regarding the composition of the fraction of the essential oil of *U. Californica* which contains umbellulone that my inferences concerning the constitution of the latter were based only on the products obtained from the pure, regenerated ketone.

β-Dihydroumbellulone.

The "umbellulone" which was submitted to the action of sodium and alcohol, both in my experiments and in those conducted by Semmler, was only a particular fraction of the essential oil. As pointed out above, this material is not pure umbellulone, but gives results on analysis which are approximately the mean of those which would be obtained for substances possessing the formulæ $C_{10}H_{14}O$ and $C_{10}H_{16}O$ respectively.

Reduction of "Umbellulone."—In an unpublished experiment conducted by Mr. Lees, he reduced 25 grams of the umbellulone fraction (b. p. 217—222°) by means of sodium and alchohol. Some resinification ensued, and only 16 grams of volatile product were obtained. This material, which distilled almost entirely at 134—135°/70 mm., and behaved towards bromine as an unsaturated substance, was converted into the acetate. The latter was fractionally distilled, and the most constant-boiling portion (11 grams), which passed over at 144—146°/70 mm., separately collected. This was analysed:

0·1480 gave 0·4004 CO_2 and 0·1344 H_2O. C = 73·8; H = 10·1.
$C_{10}H_{15}\cdot O\cdot CO\cdot CH_3$ requires C = 74·2; H = 9·3 per cent.
$C_{10}H_{17}\cdot O\cdot CO\cdot CH_3$ „ C = 75·5; H = 10·2 „

This acetate of constant boiling point was hydrolysed, and the resulting alcoholic product fractionally distilled, when the greater portion passed over between 207° and 212°. This product, when dissolved in chloroform, readily decolorised a solution of bromine in the same solvent. It was analysed with the following result:

0·0749 gave 0·2146 CO_2 and 0·0784 H_2O. C = 78·2; H = 11·6.
$C_{10}H_{16}O$ requires C = 78·9; H = 10·5 per cent.
$C_{10}H_{18}O$ „ C = 77·9; H = 11·7 „

My own experiments on the reduction of umbellulone, which were not given in full in the previous communications (*loc. cit.*), resulted as follows: 25 grams of the umbellulone fraction (b. p. 215—225°; a_D − 34°4′) gave, on reduction, 17 grams of an unsaturated, alcoholic product. This was therefore again submitted to the action of sodium and alcohol, but was recovered apparently unchanged and was still unsaturated, no loss by resinification occurring during the second treatment. The product was then fractionated, when the greater part passed over at 132—134°/70 mm., or at 208—210° under the ordinary pressure. This material had the following constants: *d* 20°/20° = 0·9307; a_D − 27°52′ in a 1-dcm. tube. On analysis:

0·0947 gave 0·2722 CO_2 and 0·0988 H_2O. C = 78·4; H = 11·5.
$C_{10}H_{16}O$ requires C = 78·9; H = 10·5 per cent.
$C_{10}H_{18}O$ „ C = 77·9; H = 11·7 „

This analysis entirely confirms the results obtained by Lees, and the only conclusion that can be drawn is that the product of the action of sodium and alcohol on the umbellulone fraction is a mixture of alcohols possessing the formulæ $C_{10}H_{16}O$ and $C_{10}H_{18}O$ respectively. The result is, in fact, such as might be expected, for the material which was reduced appeared to be a mixture of ketones possessing the formulæ $C_{10}H_{14}O$ and $C_{10}H_{16}O$ respectively.

Since the "dihydroumbellulol" described by Semmler was prepared in the above manner, and from a portion of the identical oil employed by me, it would naturally be expected to consist of a similar mixture. It is stated to have had the following constants: d $20° = 0·931$; a_D $-27°30'$ in a 1-dcm. tube, and, on analysis, gave $C = 77·37$; $H = 11·22$ per cent. These figures for the density and rotation are practically identical with those found by me, as given above, but the analysis cannot be said to agree with any formula. It is evident, however, that Semmler's preparation must have been essentially the same as that obtained by Mr. Lees and by the present author.

Oxidation of the Reduction-product.—Fifteen grams of the above-described mixture of alcohols (see Trans., 1906, **89**, 1118) gave, on oxidation with a chromic acid mixture, 6 grams of a product, boiling at 204—209°, which was designated "β-dihydroumbellulone." This material, when dissolved in chloroform, readily decolorised a solution of bromine in the same solvent, and, on analysis, gave results in agreement with those required for the formula $C_{10}H_{16}O$. This was confirmed by analysis of the semicarbazone. Since 6 grams of a ketonic product, $C_{10}H_{16}O$, had been obtained by oxidising 15 grams of a mixture of unsaturated alcohols, $C_{10}H_{16}O$ and $C_{10}H_{18}O$, it was stated that the former alcohol must have been destroyed.

The semicarbazone of this "β-dihydroumbellulone" was prepared, and was first obtained in a viscous condition, but after standing for some time it became solid. It was then dissolved in alcohol and allowed to crystallise, when a product melting at 150° was obtained. On recrystallisation from a mixture of ethyl acetate and light petroleum, the melting point of this product was raised to 155—156°. This material has now been fractionally crystallised from ethyl acetate, when the melting point of the most sparingly soluble fraction gradually rose, and eventually about 30 per cent. of the product was obtained in well-defined needles, which were sparingly soluble in ethyl acetate, and melted sharply at 204°. The ketone regenerated from this semicarbazone (m. p. 204°) behaved towards bromine as a saturated compound, and is doubtless the substance which gave rise to Semmler's benzylidene derivative. The more readily soluble portions of the semicarbazone, which formed the greater part of the material, gave a ketone which, when dissolved in chloroform, instantly decolorised a solution of bromine in the same solvent.

The name "β-dihydroumbellulone" ought therefore to be discarded, since the preparation is a mixture.

The "β-dihydroumbellulone" prepared by Semmler had the same characters as the liquid which I had described under that name, but he failed to observe that the preparation is a mixture, consisting, to a considerable extent, of an unsaturated substance. The semicarbazone obtained by him melted at 150°, and was evidently the above-described mixture.

The foregoing results may be summarised as follows:

The umbellulone obtained by the fractional distillation of the essential oil of Californian laurel is not the pure ketone, $C_{10}H_{14}O$, but, on analysis, gives results agreeing with those yielded by a mixture of substances, $C_{10}H_{14}O$ and $C_{10}H_{16}O$.

When this umbellulone fraction is reduced, it gives about 70 per cent. of its weight of an unsaturated mixture of alcohols, $C_{10}H_{16}O$ and $C_{10}H_{18}O$.

On oxidising this mixture of alcohols, the former one is readily destroyed by the excess of the oxidising agent, and less than a 50 per cent. yield of a ketonic product ("β-dihydroumbellulone"), $C_{10}H_{16}O$ is obtained.

The explanation of this appears to be that the original fraction of the oil is a mixture of ketones, $C_{10}H_{14}O$ and $C_{10}H_{16}O$, which, on reduction, yields the corresponding alcohols, that is, umbellulol and a product, $C_{10}H_{17}{\cdot}OH$. This conclusion is in agreement with the unsaturated character of the material. On treating this mixture with chromic acid, the umbellulol is broken down, and "β-dihydroumbellulone" is obtained from the product, $C_{10}H_{17}{\cdot}OH$, from which consideration it appears highly probable that "β-dihydroumbellulone" is not a derivative of the ketone from which it was named.* Finally, this "β-dihydroumbellulone" is a mixture of at least two ketones, one of which is saturated, and one unsaturated.

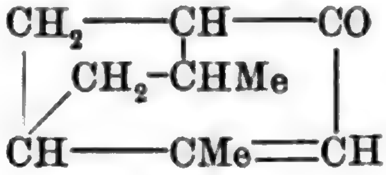
It was from a constituent of this mixture of unknown origin that Semmler prepared homotanacetonedicarboxylic acid, and such is the foundation upon which he has based his conclusions respecting the constitution of umbellulone.

Apart from the above considerations, Semmler represents "β-dihydroumbellulone" as umbellulone in which the double linking has been reduced. This view, however, could not possibly be correct, even if "β-dihydroumbellulone" were a definite derivative of umbellulone, since α-dihydroumbellulone (m. p. of semicarbazone 177°), a compound which is certainly a pure, saturated derivative of umbellulone, must be represented in this manner. α-Dihydroumbellulone is not only formed by the reduction of monobromoumbellulone (Lees, Trans., 1904, **85**, 639), but can also be obtained by the reduction, with zinc dust and acetic acid, of umbellulone dibromide, the initial product of the interaction of bromine and umbellulone at 0°.

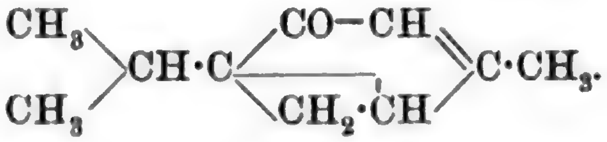
---

* With the exception of "β-dihydroumbellulone," all compounds described by Power and Lees, by Lees, or myself as derivatives of umbellulone have been proved to be derived from this ketone.

Lastly, the experimental facts recorded in my two previous communications on umbellulone prove conclusively that this ketone can only be represented either by the formula which I believe to be correct (I), and which is in harmony with the properties of umbellularic acid, or by the one preferred by Semmler (II):



(I.)



(II.)

If the latter formula were correct, it would certainly appear that tetrahydroumbellulone must be menthone, but this is not the case, as the former product, which is not an individual substance but probably consists of stereoisomerides, boils at 197—198°, and is totally devoid of mint-like odour.

It is seen therefore that the conclusions so hastily drawn by Semmler, from his experiments with a small quantity of impure umbellulone, are absolutely devoid of value, in so far as the constitution of this ketone is concerned. At the most, they may serve to indicate the nature of a ketone other than umbellulone which occurs in *Umbellularia* oil, or, in other words, the crude umbellulone may contain *l*-tanacetone or a "tanacetone of the menthone series."

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

XXIV.—*Valency.*

By JOHN ALBERT NEWTON FRIEND, Ph.D.

THAT atoms, as distinct from groups, are capable of entering into chemical combination with one another, was first realised by Frankland in 1852. Simultaneously, in 1858, Couper and Kekulé extended this view, and laid the foundation of our present theory of valency.

No theory can be regarded as complete, however, which does not explain the following phenomena.

I.—*The Valency of most Elements Apparently Varies.*

Kekulé believed that valency was constant. Thorpe's discovery of phosphorus pentafluoride (*Annalen*, 1876, **182**, 201), in which phosphorus is quinquevalent, whereas in hydrogen phosphide it is tervalent, showed that this assumption was untenable. It was argued, however, that in the latter compound the two unused valencies saturated each other. The fact that in ferrous chloride ($FeCl_2$) there is only one unsaturated valence was explained by doubling the formula. The discovery of Nilson and Petterson (*Zeitsch. physikal. Chem.*, 1888, **2**, 669), that the three chlorides of indium can exist in the gaseous state, namely, InCl, $InCl_2$, and $InCl_3$, apparently proves, however, that valency is not constant.

II.—*Electropositive Elements Readily Combine with Electronegative to form the most Stable Compounds.*

This has led several chemists to suggest electrochemical theories of valency. In 1899, Abegg and Bodländer (*Zeitsch. anorg. Chem.*, 1899, **20**, 453) discussed one such in full, but it presented several difficulties and has not been generally accepted.

III.—*Electropositive and Electronegative Elements Combine both with Themselves and with other Elements of the same Sign to Form Fairly Stable Molecules.*

This is difficult to explain if a purely electrochemical theory of valency is accepted. On the other hand, if valency is regarded merely as an attractive force existing between any two atoms, no explanation is forthcoming for the fact that elements of opposite sign combine with great readiness, whereas it has not been found possible to prepare compounds of fluorine and oxygen or fluorine and chlorine.

IV.—*Molecules can Combine with other Molecules to Form Highly Stable Complexes.*

Under this heading are classified the well-known double salts and compounds containing water of crystallisation, &c.

They were explained in an unsatisfactory manner by assuming the existence of an indefinite residual valency. Abegg (*Zeitsch. anorg. Chem.*, 1904, **39**, 331) has given expression to the view that associated molecules and molecular compounds are due to the unsaturated valencies of the atoms composing the molecules. But according to the generally accepted views on valency, the atoms in the molecules $CuSO_4$ and H_2O are saturated, nevertheless, the molecule $CuSO_4,5H_2O$ is exceedingly stable. The ammino-compounds of platinum and the allied metals, owing to their great complexity, offered unusual difficulty in the assignment of suitable structural formulæ. By a very ingenious theory, Werner has been able to divide these complexes into well-defined groups, and to give them suitable formulæ. When, however, his theory is applied to such simple compounds as ammonium chloride, it is found to be unsatisfactory.

In order to meet these and other difficulties, the author distinguishes three kinds of valency, namely, free positive, free negative, and residual or latent valency.

1.—*Free Negative Valency.*

Since hydrogen is electropositive and univalent, only those elements which possess a negative valence can combine with it. It is an interesting observation that no duly authenticated compounds are on record containing hydrogen attached to one atom of the same element in two or more proportions. Thus, whilst hydrogen phosphide and methane are easily prepared, the radicles phosphonium and methyl have resisted all attempts at isolation. Experiment seems to indicate that ammonium can exist as an amalgam with mercury, but it is not possible to prepare it in the free state (Rich and Travers, Trans., 1906, **89**, 872). As a general rule, therefore, hydrides may be regarded as trustworthy guides to the numerical value of the free negative valencies of the elements. (Exceptions to this rule are considered later.)

2.—*Free Positive Valency.*

In addition to negative, some elements possess positive valency, and may be termed amphoteric (Abegg, *loc. cit.*, p. 340). Others apparently possess only positive or only negative.

The numerical value of the positive valency is not so easily determined as that of the negative, since we have no negative element corresponding with hydrogen, which combines with one atom of any other element in only one proportion. Abegg adopts the suggestion of Mendeléeff (Ostwald's *Klassiker*, **68**, 48), and assumes that the highest oxygen compounds, omitting peroxides, give the maximal valency of the elements. Not only is this method somewhat uncertain owing to the bivalent nature of oxygen, but it is inconsistent. The valency of manganese, for example, is decided by a much higher and more unstable oxide (Mn_2O_7) than the peroxide.

The author suggests that fluorine is the most suitable element for determining the maximal positive valency of the elements. Martin (*Chem. News*, 1904, **89**, 49) has already drawn attention to the similarity of oxygen and fluorine, and the latter element possesses the decided advantage of being univalent. (The fact that at lower temperatures the hydride, HF, has the double formula, will be alluded to later.)

Chlorine, fluorine, and oxygen are the only elements which possess free negative, but no free positive valencies. Metals apparently possess free positive valency alone. A list of all the amphoteric elements, together with their fluorides and hydrides, is given in the adjoining table. The fact that in nearly every case the sum of the free valencies is eight is very remarkable. Some chemists have assumed that every element possesses eight valencies (Abegg, *loc. cit.*; Morozoff, *J. Russ. Phys. Chem. Soc.*, 1906, **38**, ii, 481). The assumption is not borne out, however, in the case of the inert gases and the alkali metals. Although no fluoride of nitrogen has as yet been isolated, this element is regarded as amphoteric, for reasons which appear in the sequel.

Amphoteric Elements.[1]

Element.	Hydride.	Free negative valency.	Fluoride.	Free positive valency.	Total free valency.
Antimony......	SbH_3	3.	SbF_5[2]	5	8
Arsenic	AsH_3	3	AsF_5[3]	5	8
Boron	BH_3	3	BF_3[4]	3	6
Bromine	BrH	1	BrF_3[5]	3	4
Carbon	CH_4	4	CF_4[6]	4	8
Iodine	IH	1	IF_5[7]	5	6
Nitrogen	NH_3	3	NOF[11]	3	6
Phosphorus ...	PH_3	3	PF_5[8]	5	8
Selenium	SeH_2	2	SeF_6[9]	6	8
Silicon	SiH_4	4	SiF_4[12]	4	8
Sulphur	SH_2	2	SF_6[10]	6	8
Tellurium......	TeH_2	2	TeF_6[9]	6	8

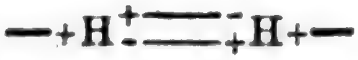
[1] Contrast Abegg (*loc. cit.*, 340). [2] Ruff and Plato (*Ber.*, 1904, **37**, 673).
[3] Ruff and Graf (*Ber.*, 1906, **39**, 67).
[4] Gay Lussac and Thenard (*Ann. Chim. Phys.*, 1809, **69**, 204).
[5] Prideaux, (Proc., 1905, **21**, 240).
[6] Moissan (*Compt. rend.*, 1890, **110**, 276, 951).
[7] Gore (*Chem. News*, 1871, **24**, 291). [8] Thorpe (*loc. cit.*).
[9] Prideaux (Trans., 1906, **89**, 316).
[10] Moissan and Lebeau (*Compt. rend.*, 1900, **130**, 865).
[11] Ruff and Stäuber (*Zeitsch. anorg. Chem.*, 1905, **47**, 190).
[12] Gay Lussac and Thenard (Gilbert's *Annalen*, 1809, **32**, 1).

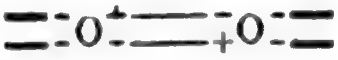
3. *Residual or Latent Valency.*

By residual or latent valency the author understands positive and negative valencies, which differ from the above mentioned free valencies in that *they can only be called out in pairs of equal and opposite sign.* They do not differ in their chemical nature, however, as will be shown in the sequel.

Since positive valencies cannot unite with positive, or negative with negative, it is necessary to assume the existence of this latent valency to explain the formation of diatomic or polyatomic molecules either of the same element or of different elements of the same sign.

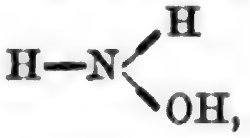
Thus the molecules of hydrogen and oxygen are represented by the schemes:





In order to distinguish between the free and latent valencies, it is suggested that the former be represented by thicker lines, as above. It is assumed that the latent valencies, when not in actual use, saturate themselves, whereas the free valencies in similar circumstances remain unsaturated.

It is not necessary for all the free valencies to be saturated before the latent valencies are called out. Thus, in a molecule of hydrogen no free valencies are saturated, and in hydroxylamine,



two negative valencies remain unsaturated.

Every element may be considered to possess latent valencies, although these differ very much in intensity, probably due to their tendency to saturate themselves. In the case of the metals, they are too weak to hold the atoms together in the vaporous condition, yet very stable alloys are formed through their agency at low temperatures.

In the metallic hydrides combination is presumably effected by the latent valencies, for example, —K═H—, and this accounts for their instability.

The latent valencies of hydrogen are so weak that it is never known to function as a bi- or ter-valent element (contrast chlorine); we might therefore expect its molecule to be easily dissociated. That such is not the case, however, is due to the fact that the stability of a molecule depends, not merely on the force of attraction between the atoms, but on the relation between that force and the weight of the atoms. This is well illustrated by the halogens. Iodine vapour readily dissociates, and at 1000°, one-third of the molecules are monatomic, whilst at 1700° dissociation is complete (V. Meyer, *Ber.*, 1880, **13**, 394; Biltz and V. Meyer, *Ber.*, 1889, **22**, 725). Chlorine, on the other hand, with an atomic weight of less than one-third that of iodine, shows no appreciable dissociation even at 1200° (Crafts, *Ber.*, 1883, **16**, 457).

In the case of the inert gases, the latent valency is so weak that the molecules are monatomic even at atmospheric temperatures (Ramsay and Travers, *Proc. Roy. Soc.*, 1900, **67**, 329). It is just possible that if the densities were determined at temperatures near their boiling points, indications of association to diatomic molecules might be observed.

From the above it is clear that the elements fall into four groups, namely, those which possess, in addition to latent valencies:

1. Free positive valency only—Hydrogen and the metals.
2. Free negative valency only—Fluorine, chlorine and oxygen.

3. Free positive and free negative valencies—Amphoteric elements.

4. No free valencies—The inert gases.

In order to illustrate this theory, it will now be considered in its application to a few special cases.

Fluorine.

Since no compound of oxygen and fluorine is capable of existence, it is assumed that neither element possesses free positive valency.

Brauner's assumption that the activity of fluorine is due to its molecules being monatomic (*Zeitsch. anorg. Chem.*, 1894, **7**, 12) has been shown by Moissan (*Compt. rend.*, 1904, **138**, 728) to be untenable. The present author suggests that *the activity of fluorine is due to its univalent nature, and the entire absence of free positive valency.* This explains the analogy between oxygen and fluorine (Martin, *loc. cit.*), the weaker character of the former being due to the mutually repellent action of its two free valencies. Mallet has shown that at about 30° the molecule of hydrofluoric acid is double (*Chem. News*, 1881, **44**, 164), a result which has been confirmed by Thorpe and Hambly (Trans., 1889, **55**, 163). According to the author's notation the formula is $\mathrm{H{-}F{=}F{-}H}$, in which fluorine functions as a tervalent element.

Chlorine.

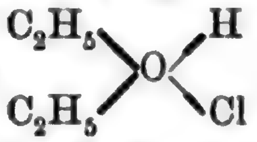
No evidence of the existence of a compound of chlorine and fluorine has been obtained, although Lebeau has brought these elements into contact at $-182{\cdot}5°$ (*Compt. rend.*, 1906, **143**, 425).

Chlorine, therefore, possesses no free negative valency. The fact that it is not so active as fluorine may be ascribed to its greater atomic weight; perhaps also to the greater activity of its latent valencies, which enable it to combine with oxygen.

Hypochlorous acid may be represented by the formula $\mathrm{H{-}Cl{=}O{=}}$, which explains the ease with which oxygen is split off.

Oxygen.

Collie and Tickle (Trans., 1899, **75**, 710), after a study of the hydrochloric acid salt of dimethylpyrone, were the first to point out that oxygen could function as a quadrivalent element. Since then various organic compounds have been prepared in which the valency of oxygen is undoubtedly four. They all consist, however, *in adding two elements or groups of elements to the oxygen in such a way as to saturate* *a positive and a negative valence and never two of the same kind*, for example,

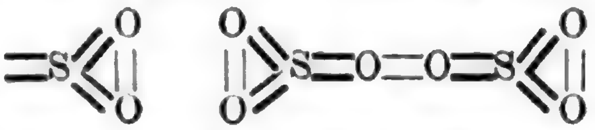


.

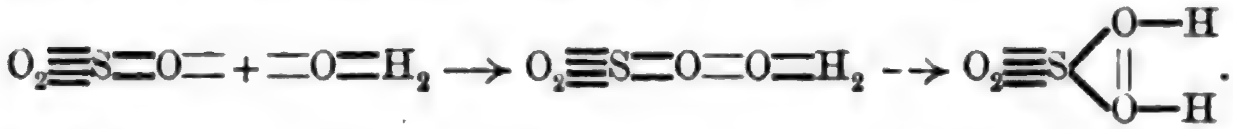
According to the author's theory, this is precisely what we should expect, since on saturating the two negative valencies of the oxygen, only latent valencies remain. The structural formula above shows perfect analogy to ammonium compounds (see later). The term oxonium as applied to these salts receives, therefore, full justification.

We have evidence to show that water is associated, although to what extent is not definitely known, for all the methods which have been employed to determine its association are open to criticism (compare Ramsay and Shields, *Zeitsch. physikal. Chem.*, 1893, **12**, 434; Vernon, *Chem. News*, 1891, **64**, 54, &c.). If the molecules are double, the formula is clearly $H_2{=}O{=}O{=}H_2$. If of a higher order, the oxygen atoms are presumably arranged in a ring. The association of phenols, alcohols, and acetic acid may be explained in an analogous manner.

An interesting case is that afforded by sulphur trioxide, which exhibits a strong tendency to associate to double molecules (Oddo, *Gazzetta*, 1901, **31**, ii, 158), whereas sulphur dioxide does not. In the latter case, the latent valencies of one oxygen atom saturate those of the other. Hence association is only likely to take place between the valencies of the sulphur atom. This is rendered the less probable since two positive valencies of the latter are still unsaturated, and would tend to cause a repulsion between two sulphur atoms. In sulphur trioxide, the latent valencies of the third oxygen atom are not externally saturated and association becomes easy. Thus:



Since $[SO_3]_2$ is sparingly soluble in water, it would seem that the solubility depends partly on the oxygen atoms. The author suggests that when (SO_3) dissolves in water, an intermediate hydrate is formed, which then undergoes rearrangement to form sulphuric acid. Thus:



The fact that water crystallises alone with its salts is also to be ascribed to the latent valencies of the oxygen. We might therefore expect other substances possessing bivalent oxygen, and a similar structure to water, for example, ether or alcohol, to crystallise out in the same way. This is well known to be the case, for example,

$$CaCl_2,4CH_3{\cdot}OH.$$

Engler and Wild (*Ber.*, 1897, **30**, 1669) conclude, as the result of many experiments, that when the alkali metals are oxidised in the air there is a direct combination of the metals with the oxygen molecule, a peroxide being formed which slowly reacts with water, forming hydrogen peroxide and the metallic hydroxide. According to the theory of valency under discussion this receives a ready explanation. Combination of the metal with the oxygen molecule is not due to the breaking of one of the bonds holding the oxygen atoms together, as the generally accepted theory demands. It is due to the union of the free valencies of one oxygen atom with those of the sodium atoms. Thus:

$$2\mathrm{Na}{=} + {=}\mathrm{O}{=}\mathrm{O}{=} \longrightarrow \mathrm{Na}_2{=}\mathrm{O}{=}\mathrm{O}{=}$$

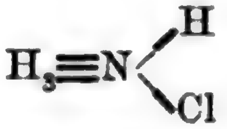
This explains the ease with which the second atom of oxygen is split off.

The assumption that the whole oxygen molecule takes part in many other cases of oxidation is strongly supported by the recent work of Manchot (*Annalen*, 1902, **325**, 95) and Bach (*Compt. rend.*, 1897, **124**, 2, 951). It is unnecessary to discuss these cases, as the principle is identical throughout.

Nitrogen.

The study of the valency of nitrogen is one of particular interest. Although it forms no compound with fluorine alone, the author regards it as amphoteric on account of the great stability of its oxygen compounds. As is true of most of the other amphoteric elements, the free positive valencies of nitrogen cannot be called into action, when some or all of its free negative valencies are saturated, and vice versa. An exception to this rule is carbon.

In ammonia the free negative valencies of nitrogen are saturated. It is clear that a fourth negative valence can only be called out in conjunction with a positive. This explains why all attempts to isolate ammonium have failed (see p. 262). If, however, the positive latent valence can be saturated, the problem is solved, for example, ammonium chloride,



We may assume that when ammonia and hydrochloric acid come into contact, the compound $\mathrm{H_3N{=}ClH}$ is formed, which undergoes re-arrangement (compare Cain's formula, *Mem. Manchester Phil. Soc.*, 1904, **48**, xiv.).

It does not follow that when ammonium chloride dissociates, the *same* hydrogen atom combines again with the chlorine. Since on saturation free and latent valencies of the same sign become identical, any other atom of hydrogen in the molecule stands an equal chance, and the valence with which the nitrogen held it now saturates the positive valence and becomes latent. It is thus unnecessary to adopt the cube theory of van't Hoff (*Ansichten über die organische Chemie*, p. 79) to which H. O. Jones has taken exception on stereoisomeric grounds (Trans., 1903, **83**, 1403; 1905, **87**, 1721).

It will be seen that ammonia and water are alike in that the oxygen and nitrogen atoms are saturated by hydrogen, and both elements can combine with other atoms or groups by means of their latent valencies only. This affords a simple explanation of the fact that ammonia and water are frequently interchangeable in chemical compounds, for example, $CuSO_4,5H_2O$ and $CuSO_4,5NH_3$. Further, Brill has shown that liquid ammonia is slightly associated although not to the same extent as water (*Ann. Physik*, 1906, [iv], **21**, 170).

It has already been pointed out that organic compounds of bivalent oxygen, for example, alcohols, can, like water, crystallise with inorganic salts. The same property is exhibited by organic derivatives of tervalent nitrogen. For example, a large number of salts has been prepared by Lang (*Ber.*, 1888, **21**, 1578) Pincussohn (*Zeitsch. anorg. Chem.*, 1897, **14**, 379), and others, containing pyridine of crystallisation. A most remarkable example is that afforded by cuprous chloride.

In the presence of water this salt can absorb carbon monoxide, but not when perfectly dry. Lang found, however, that its solution in pyridine absorbs this gas with ease. Manchot and Friend * have since shown that not only may pyridine be replaced by other derivatives of tervalent nitrogen, for example, aniline, *o*-toluidine, and piperidine, but that the amount of carbon monoxide absorbed per molecule of cuprous chloride is identical in each case with that absorbed in the presence of water. According to the usual theory of valency this remarkable analogy cannot be satisfactorily explained.

Since ammonia gas dissolves in water with evolution of a considerable amount of heat, it is generally assumed that ammonium hydroxide is the chief product, despite the comparatively poor conductivity. Since such a solution always has a strong odour of ammonia, the author suggests that on mixing ammonia and water, a hydrate is first formed, as in the case of sulphur trioxide (see p. 266), and that only part of this undergoes rearrangement to form the isomeric ammonium hydroxide. In the solution we have, therefore, equilibrium between these two substances and ammonium ions. Thus:

$$H_3\equiv N=O=H_2 \rightleftarrows NH_4OH \rightleftarrows NH_4^{\cdot} + OH'.$$

That the negative latent valence does not differ in chemical nature from the free negative valencies may be deduced from the work of Victor Meyer. This investigator showed that dimethyldiethylammonium iodide prepared from dimethylamine and ethyl iodide, was identical with that produced from diethylamine and methyl iodide. In the latter case, where diethylamine is employed, both the ethyl groups are attached by free negative valencies to the nitrogen. Hence one of the methyl groups in the final product must be attached by a latent negative valence. In the second case, however, it is equally clear that a methyl group must be attached in the same way. Hence it follows that the free and the latent negative valencies of nitrogen do not differ in quality. Other experiments lead to similar conclusions with regard to the valencies of sulphur in the sulphonium compounds. It may therefore be assumed that in all cases, *latent and free valencies possess the same chemical nature.*

---

* *Annalen*, 1908 [in the press].

Carbon.

As might be expected from its position in the periodic classification, carbon functions largely as a neutral element. Its total free valency is 8, but no compound is known in which more than four of these valencies are used at once. Apparently it is immaterial which valencies are called out. They may be all positive (CF_4), all negative (CH_4), or a mixture of positive and negative in any of the three possible proportions ($CHCl_3$, CH_2Cl, CH_3Cl). Carbon is therefore a perfect example of an amphoteric element.

No compounds are known in which carbon functions as a univalent element, and we have no proof that it is ever truly bivalent. Carbon monoxide may be explained on the assumption that the two free valencies of the oxygen, together with two latent valencies, saturate the four free valencies of the carbon atom. A similar explanation holds in the case of hydrocyanic acid and fulminic acid (compare Nef, *J. Amer. Chem. Soc.*, 1904, **26**, 1549). Gomberg's discovery of triphenylmethyl (*Ber.*, 1900, **33**, 3150) seems to indicate that carbon can function as a tervalent element.

Werner's Theory.

It will be at once apparent that the author's free valencies correspond to the principal valencies of Werner, and the latent valencies to the auxiliary. The last two, however, are very dissimilar in properties.

According to Werner's theory, elements or groups attached by auxiliary valencies are not capable of dissociation (*Neuere Anschauungen auf dem Gebiete der Anorganischen Chemie,* Werner, 1905, p. 59).

Thus in ammonium chloride $[NH_3{\cdot}H{\cdot}]Cl$ one hydrogen differs from the others in being attached to the nitrogen atom by an auxiliary valence whereas no such difference in reality exists. According to the present author's theory, however, there is no such distinction between the valencies, and elements attached by latent bonds are as easily dissociable as when attached by free.

In a future paper the author hopes to discuss more in detail the bearing of his theory on that of Werner and on the ammonium compounds.

In conclusion, he has great pleasure in thanking Mr. W. E. S. Turner, M.Sc., for many useful criticisms and suggestions.

XXV.—*The Oxidation of Aromatic Hydrazines by Metallic Oxides, Permanganates, and Chromates.*

By Frederick Daniel Chattaway.

The extraordinary ease with which aromatic hydrazines are destroyed by oxidising agents has been referred to by most chemists who have worked on them,* and diazonium salts have been universally regarded as the primary products of their oxidation.

The behaviour of these substances when oxidised by free oxygen in alkaline solution (Chattaway, Trans., 1907, **91**, 1323) having made this generally accepted view seem improbable, a number of experiments have been carried out on their oxidation in presence of alkalis by various metallic oxides and highly oxygenated salts. The results may be stated in general terms as follows.

Primary aromatic hydrazines are readily attacked by most substances capable of giving up oxygen at all easily, the products being in the main the same as when free oxygen is used.

The action which takes place to a predominating extent causes the liberation of nitrogen and the replacement of the hydrazino-group by hydrogen. This main action is generally accompanied by secondary ones, which take place to a comparatively very small, but varying, extent; hydrocarbons of the diphenyl group containing two of the aromatic residues linked together are produced, a little tarry matter is frequently formed, and sometimes, in still smaller quantity, simple azo-derivatives, as, for example, azobenzene. Phenols may be formed in small quantity, but only when the oxidising agent employed acts very energetically. Diazo-compounds are never produced when the oxidation is carried out in alkaline solution, but only in presence of a considerable excess of some strong acid. Azoimides are formed when alkalis are absent and the hydrazines are present in excess.

---

* Compare Fischer, *Annalen*, 1878, **190**, 67, and 1879, **199**, 281; Fischer and Ehrhard, *Annalen*, 1879, **199**, 333; Haller, *Ber.*, 1885, **18**, 90; Zincke, *Ber.*, 1885, **18**, 786; Strache, *Monatsh.*, 1891, **12**, 523, and 1892, **13**, 316; Wurster, *Ber.*, 1887, **20**, 2633.

The nature of the oxidising agents and the conditions of the experiments naturally affect the rate of action. All oxides act more vigorously when hydrated and when finely divided, and action becomes much more rapid as the temperature is raised.

If the basic oxide of the metal is easily reduced, the metal itself is liberated, as with the oxides of mercury, copper, and silver; in other cases, the peroxides only act, and the basic oxide is formed, as with the peroxides of lead and manganese.

Alkaline permanganates act very energetically at the ordinary temperature, whilst with chromates the temperature has to be raised considerably before any appreciable evolution of nitrogen occurs.

Potassium chromate oxidises all primary aromatic hydrazines very easily, giving a practically theoretical yield of nitrogen and hydrocarbon, and being itself reduced to potassium and chromium hydroxides. This reaction affords the most convenient method yet described for replacing a hydrazino- or amino-group by hydrogen, the latter being first converted into the former through a diazonium salt.

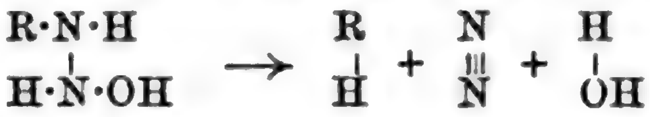
If the reduction of copper oxide by phenylhydrazine is carried out under suitable conditions, the metal set free can be deposited on glass in the form of a coherent metallic film, equalling in brilliancy a similarly deposited film of silver, and showing the splendid red colour of polished copper.

The view of the course of the reaction recently put forward to explain the oxidation of hydrazines by free oxygen (Chattaway, Trans., 1907, **91**, 1323) affords, with a suitable extension, a simple explanation of all the facts observed.

When either oxygen or an oxidising agent acts on a primary aromatic hydrazine, one of the hydrogen atoms of the hydrazino-group is first attacked, and a hydroxyhydrazine is produced,* thus:

$$R\cdot NH\cdot NH_2 + O = R\cdot NH\cdot NH\cdot OH.$$

This substance, however, not being stable in presence of alkalis, undergoes disruption during some phase of its motion, thus:



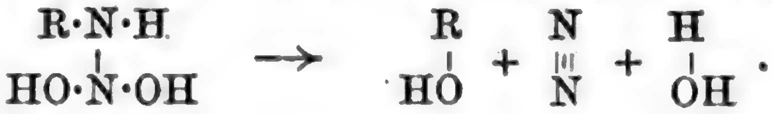
$$\begin{array}{c} R\cdot N\cdot H \\ | \\ H\cdot N\cdot OH \end{array} \longrightarrow \begin{array}{c} R \\ | \\ H \end{array} + \begin{array}{c} N \\ ||| \\ N \end{array} + \begin{array}{c} H \\ | \\ OH \end{array}$$

the splitting off of hydrocarbon and water occurring either in one or two stages.

If, however, a very energetic oxidising agent is used, a certain number of molecules may, before breaking down, undergo a further oxidation, a second hydrogen atom being thus replaced by another hydroxyl group. The similar breaking down of this molecule under the influence of the alkali results in the formation of a phenol:

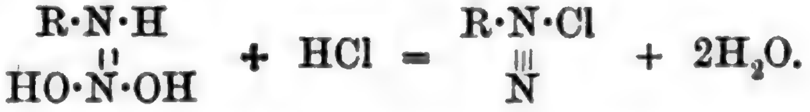
---

* Probably the action which first takes place is the addition of two hydroxyl groups to the nitrogen which thus develops its quinquevalency.



$$\begin{array}{c}R\cdot N\cdot H\\ |\\ HO\cdot N\cdot OH\end{array} \longrightarrow \begin{array}{c}R\\ |\\ HO\end{array} + \begin{array}{c}N\\ |||\\ N\end{array} + \begin{array}{c}H\\ |\\ OH\end{array}.$$

In the absence of an alkali which acts as catalytic agent and much accelerates the decomposition of these hydroxyhydrazines, the introduction of the second hydroxyl group takes place to a much greater extent, and in the presence of a strong acid at a low temperature a diazonium salt may be formed, thus:

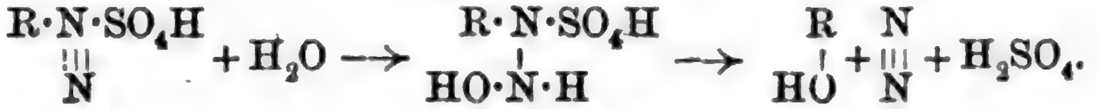


$$\begin{array}{c}R\cdot N\cdot H\\ \|\\ HO\cdot N\cdot OH\end{array} + HCl = \begin{array}{c}R\cdot N\cdot Cl\\ |||\\ N\end{array} + 2H_2O.$$

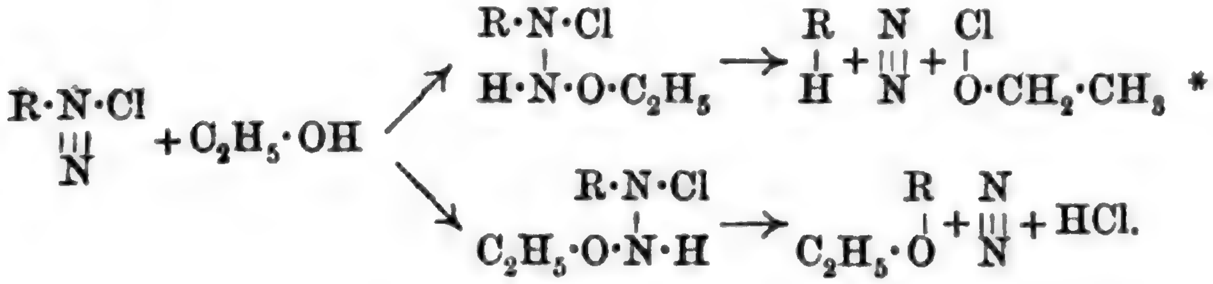
The subsidiary reactions, for example, the production of hydrocarbons of the diphenyl series and of azo-derivatives in presence of alkalis or of azoimides in absence both of alkalis and of acids, can be simply explained by the interaction of two molecules of the hydroxyhydrazines primarily formed. Among the products of the oxidation of primary aromatic hydrazines in presence of alkalis, even when carried out at a low temperature, no diazo-compounds can be detected. This makes it highly improbable that they are ever formed, the breaking down of the oxidised molecule taking place at a stage in the oxidation before the one at which they could be produced. The production of phenols in small quantity when energetic oxidising agents are used shows that, even if this second stage is reached and two hydroxyl groups are introduced into the molecule, it does not split off water in presence of alkalis, but undergoes the same type of decomposition as when only one such group is present.

This is in agreement with the well-known behaviour of diazonium compounds, these only undergoing the characteristic diazo-decompositions in presence of agents able to form additive compounds with them; for example, water, alcohol, or cuprous chloride, thus giving to the molecule a structure analogous to that of the hydroxy-compounds figured above.

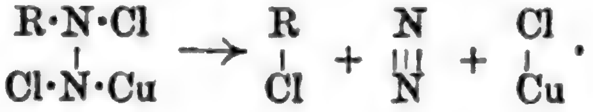
It is unnecessary to assume as Hantzsch does (*Ber.*, 1900, **33**, 2517) that this addition is followed immediately by a partial decomposition resulting in the formation of an unstable *syn*-diazo-compound which then breaks down. A much more probable explanation is that diazo-compounds as such do not break down with elimination of nitrogen, this only taking place in a molecule where each nitrogen atom carries at least two suitably related groups attached to it, the single linking of the nitrogen atoms now giving the mobility necessary for re-arrangement of the molecule before its disruption. Thus taking three examples, we should represent the introduction of a hydroxyl group, an ethoxyl group, or a hydrogen atom and a chlorine atom thus:



$$\begin{array}{c}R\cdot N\cdot SO_4H\\ \vert\vert\vert\\ N\end{array} + H_2O \longrightarrow \begin{array}{c}R\cdot N\cdot SO_4H\\ \vert\\ HO\cdot N\cdot H\end{array} \longrightarrow \begin{array}{c}R\\ \vert\\ HO\end{array} + \begin{array}{c}N\\ \vert\vert\vert\\ N\end{array} + H_2SO_4.$$



$$\begin{array}{c}R\cdot N\cdot Cl\\ \vert\vert\vert\\ N\end{array} + C_2H_5\cdot OH \begin{array}{l}\nearrow \begin{array}{c}R\cdot N\cdot Cl\\ \vert\\ H\cdot N\cdot O\cdot C_2H_5\end{array} \longrightarrow \begin{array}{c}R\\ \vert\\ H\end{array} + \begin{array}{c}N\\ \vert\vert\vert\\ N\end{array} + \begin{array}{c}Cl\\ \vert\\ O\cdot CH_2\cdot CH_3\end{array}\ ^{*}\\ \searrow \begin{array}{c}R\cdot N\cdot Cl\\ \vert\\ C_2H_5\cdot O\cdot N\cdot H\end{array} \longrightarrow \begin{array}{c}R\\ \vert\\ C_2H_5\cdot O\end{array} + \begin{array}{c}N\\ \vert\vert\vert\\ N\end{array} + HCl.\end{array}$$



$$\begin{array}{c}R\cdot N\cdot Cl\\ \vert\\ Cl\cdot N\cdot Cu\end{array} \longrightarrow \begin{array}{c}R\\ \vert\\ Cl\end{array} + \begin{array}{c}N\\ \vert\vert\vert\\ N\end{array} + \begin{array}{c}Cl\\ \vert\\ Cu\end{array}.$$

The views here advanced afford an insight into what occurs in a number of reactions which have hitherto received no satisfactory explanation, to give an instance, the behaviour of diazonium salts on reduction.

As is well known when diazonium salts are reduced by stannous chloride in presence of a large excess of hydrochloric acid, they are converted practically quantitatively into hydrazines, this being a common method of preparing the latter compounds (Meyer and Lecco, *Ber.*, 1883, **16**, 2976). When, however, an excess of acid is not used, reduction by stannous chloride gives rise to a number of quite different products, in which the aryl group present in the diazonium salt is united with hydrogen, chlorine, hydroxyl, amidogen, or the azoimide complex (Culmann and Gasiorowski, *J. pr. Chem.*, 1889, [ii], **40**, 97; Effront, *Ber.*, 1884, **17**, 2329); to take the simplest case, whilst benzenediazonium chloride yields chiefly benzene, considerable quantities of chlorobenzene, phenol, aniline, and phenylazoimide are also produced.

Again, when a diazonium salt is treated with an excess of caustic alkali and then reduced by a strongly alkaline solution of stannous oxide, nitrogen is vigorously evolved and the diazonium group is replaced by hydrogen, whilst an azo-derivative is formed in small quantity (Friedländer, *Ber.*, 1889, **22**, 587); for example, benzenediazonium chloride thus reduced yields benzene mixed with about one-tenth of its weight of azobenzene (Koenigs and Carl, *Ber.*, 1890, **23**, 2672). Complete conversion of a diazonium salt into a hydrazine by reduction, or of a hydrazine into a diazonium salt by oxidation, is only possible in presence of excess of acid, whilst complete elimination of the nitrogen and replacement of the hydrazine or diazonium group by hydrogen through the agency of oxidising or reducing agents respectively is only possible in presence of excess of alkali.

---

* The aldehyde and hydrogen chloride liberated are, without any doubt, formed by the breaking down of ethyl hypochlorite, $CH_3\cdot CH_2\cdot OCl \longrightarrow HCl + CH_3\cdot CHO$. This change can be followed when a nitrogen chloride is decomposed by alcohol.

When neither acid nor alkali is present in excess, the compounds produced in the oxidation of hydrazines are exactly those obtained in the reduction of diazonium salts.

These actions can all be satisfactorily explained by the assumption of the formation in each of them of the same type of intermediate compound, a hydroxyhydrazine which is relatively stable in presence of strong acids, but which immediately undergoes the typical diazo-decomposition in presence of alkalis. The actions by which azoimides and anilines and azo-derivatives are formed, although more complex, because requiring the interaction of two molecules of the hydroxyhydrazine, only involve intramolecular rearrangements of exactly the same type.

Oxidation of Phenyl-, o-*Tolyl-,* p-*Tolyl-,* p-*Bromophenyl-, a-Naphthyl- and β-Naphthyl-hydrazine by Metallic Oxides.*

As phenylhydrazine is much more readily attacked than the others, and as the actions which take place are typical, the behaviour of the various oxides with it alone are described.

To ascertain the action of anhydrous oxides, the finely-divided solid was suspended in about twenty times its weight of water and the calculated amount of phenylhydrazine added, the liquids being shaken for a few moments to mix them thoroughly. The hydroxides were prepared immediately before adding the phenylhydrazine by decomposing a salt of the metal dissolved in about twenty times its weight of water with the calculated quantity of potassium hydroxide.

The action of dry precipitated mercuric or mercurous oxide or the corresponding hydroxides on phenylhydrazine is very vigorous; much heat is developed, benzene is formed, and nitrogen liberated so rapidly that the liquid froths violently. The action of crystalline mercuric oxide, although vigorous, is not so violent.

Both dry and freshly precipitated silver oxide act less energetically on phenylhydrazine than the corresponding mercury compounds, the same products resulting.

Freshly-precipitated cupric hydroxide decomposes phenylhydrazine similarly, the liquid becomes warm, benzene is formed, and nitrogen is given off rapidly. Dry cupric or cuprous oxide acts much more slowly, and even on boiling the liquid very little evolution of of nitrogen is noticed.

In all these cases, the oxide is completely reduced and the metal is set free.

Lead peroxide acts immediately on phenylhydrazine, the liquid becomes warm, nitrogen is evolved with effervescence, and the peroxide is reduced to the basic oxide, whilst benzene together with a little azobenzene and diphenyl are produced. Red lead, however, has very slight action on phenylhydrazine. Manganese dioxide acts somewhat less readily than lead dioxide; the products of the oxidation, however, are the same, and the dioxide is similarly reduced to the basic oxide.

Phenylhydrazine is also oxidised by ferric hydroxide, but the action is very slow.

When copper oxide is thus reduced by phenylhydrazine, the metal, under suitable conditions, can be deposited on the glass in the form of a fine mirror. If small fragments of oxidised copper wire are heated on a water-bath for some considerable time in a saturated aqueous solution of phenylhydrazine, although the evolution of nitrogen is so slow that it can scarcely be noticed, copper is deposited on the glass immediately underneath the fragment in small, brilliant patches. By moving the pieces of oxide about, a copper mirror can be obtained of considerable size, but not of uniform brightness. If to an aqueous solution of phenylhydrazine saturated at 100° and gently boiling in a clean, new flask there is added a little potassium hydroxide and then, in very small quantities, finely-divided black copper oxide, obtained by heating the nitrate, a rapid evolution of nitrogen takes place and a small quantity of the oxide passes into solution. In this solution, the metal exists in the cuprous state dissolved in the phenylhydrazine, and can be precipitated as cuprous hydroxide by the addition of excess of potassium hydroxide. If such a solution is gently boiled and more solid oxide added from time to time as it dissolves, a very fine copper mirror can be obtained, the whole interior of the flask becoming slowly coated with a firm coherent film of the metal similar to the film of silver obtained when silver oxide is reduced by aldehydes or tartrates. It is, however, somewhat difficult to obtain a good deposit by this method, and it is easier to employ a solution of cupric hydroxide in ammonia.

The following procedure, which resembles that employed in silvering glass, gives a uniformly excellent result. Heat a mixture of one part of freshly distilled phenylhydrazine and two parts of water until a clear solution is obtained, and to this add about half its bulk of a warm saturated solution of cupric hydroxide in strong ammonia. Nitrogen is freely evolved during the addition, and the cupric is reduced to cuprous hydroxide, which remains dissolved in the ammoniacal liquid and does not undergo any immediate further reduction. Add next a hot 10 per cent. solution of potassium hydroxide until a slight permanent precipitate of cuprous hydroxide is produced. If this colourless or pale yellow liquid be now cautiously heated in contact with a perfectly clean glass surface, metallic copper is deposited on it in the form of a thin, coherent, perfectly reflecting lamina. To obtain a film of sufficient thickness, it is best not to pour off the warm reducing fluid, but to allow it to remain in the flask until quite cold. When the liquid is poured off, the film of copper should be well washed first with water, and afterwards with alcohol and ether. It should then be protected from the slow oxidising action of the air by one or two coats of some quickly drying varnish.

Oxidation of Hydrazines by Potassium Permanganate.

Aromatic hydrazines are very readily oxidised by potassium permanganate either in the presence of acids or alkalis. In presence of a small quantity of sulphuric acid, a complicated series of actions occurs. Although simple hydrocarbons and nitrogen are the main products, hydrocarbons analogous to diphenyl and azo-derivatives are formed in small quantity, whilst a considerable amount of tar is produced. Some chloro-substituted hydrocarbon may be formed if hydrochloric instead of sulphuric acid is present.

It is possible that diazonium compounds are formed in these reactions, but, if so, they must be produced in very small amount, as in spite of careful search they could not be recognised with certainty.

To give the details of one experiment, 2·7 grams of phenylhydrazine were dissolved in 30 grams of sulphuric acid diluted with 200 c.c. of water. This solution, cooled to 0°, was poured over 500 grams of crushed ice, and to it was added a similarly cooled solution of 3·2 grams of potassium permanganate in 500 c.c. of water. Considerable effervescence occurred, and benzene could be recognised by its odour; the red colour of the permanganate completely disappeared, and a small quantity of a brown solid, probably manganese dioxide, separated. A cold saturated solution of potassium hydroxide was next added until the liquid showed a strongly alkaline reaction. It was then filtered, the temperature of the liquid near being allowed to rise above 0°. To the clear, cold alkaline liquid a solution of 4 grams of β-naphthol in a slight excess of dilute potash was added. No red colour was produced, nor did any develop on allowing the liquid to stand for twenty-four hours.

The oxidation of hydrazines by permanganate in presence of alkalis, on the other hand, follows a simple course.

All primary aromatic hydrazines are readily oxidised at the ordinary temperature by an aqueous solution of potassium permanganate made alkaline with potassium hydroxide. As when other oxidising agents are used considerable rise of temperature takes place, the hydrazino-group is replaced by hydrogen, and nitrogen is rapidly evolved. A little of some hydrocarbon of the diphenyl group is produced, and some azo-derivative is formed together with a varying quantity of tarry matter. The permanganate, if in excess, is reduced to manganese dioxide, whilst the latter is further reduced to manganous oxide by excess of the hydrazine.

The amount of each of these products formed was determined in a number of cases, but the quantitative results obtained are of little importance.

The action of alkaline permanganate on phenylhydrazine, *p*-bromophenylhydrazine, and *o*- and *p*-tolylhydrazine has been studied.

On adding phenylhydrazine to an excess of a saturated solution of potassium permanganate, made strongly alkaline with potassium hydroxide, until the red colour of the permanganate disappeared, a violent evolution of nitrogen took place, and the temperature of the liquid rose considerably. All the benzene formed could not be collected, since much was carried away in the form of vapour by the rapidly escaping nitrogen. When violent action was over, the remainder of the benzene was driven off in a current of steam; on continuing the passage of steam for some time, a small quantity of diphenyl and a considerable amount of azobenzene slowly distilled over. On separating the manganese dioxide, acidifying the strongly alkaline filtrate with sulphuric acid, and extracting with ether, a very small quantity of an oily, strongly smelling substance, apparently phenol, was obtained; the amount, however, was so small that it could not be identified with certainty.

Similar experiments, using an excess of phenylhydrazine and a known quantity of permanganate, did not yield constant quantitative results.

Several attempts were made to discover if a diazo-compound is produced in the action, but without result, the amount of such compound if it is produced at all must therefore be very small.

To give the details of one experiment, 4·2 grams of potassium permanganate and 10 grams of potassium hydroxide were dissolved in 400 c.c. of water, the solution was cooled to 0°, and poured over 200 grams of crushed ice. To this was added a similarly cooled solution of 5 grams of phenylhydrazine and 10 grams of potassium hydroxide in 400 c.c. of water. As the hydrazine solution was added, nitrogen was rapidly given off, the odour of benzene became evident, and the red permanganate solution became first green from the production of manganate and finally brownish-black from the deposition of hydrated manganese dioxide. The addition of the phenylhydrazine solution was continued until the green colour just disappeared. The manganese dioxide was then filtered off, and the clear, cold alkaline liquid mixed with a solution of 4 grams of β-naphthol in a slight excess of aqueous potassium hydroxide. Not the slightest red colour was produced, nor did any develop on allowing the liquid to stand for twenty-four hours.

The amounts of diphenyl and azobenzene formed were ascertained by reducing a known weight of the mixture and determining the amount of diphenyl remaining.

The other hydrazines mentioned behave with potassium permanganate similarly to phenylhydrazine.

Oxidation of Hydrazines by Alkaline Dichromates and Chromates.

Hydrazines are readily oxidised by dichromates at the ordinary temperature, and by chromates if the temperature is somewhat raised. In each case, the action is a simple one, the dichromate and chromate alike being converted into alkaline hydroxide and hydrated chromium sesquioxide, whilst the hydrazine yields the hydrocarbon or substituted hydrocarbon and nitrogen. A very little diphenyl or other hydrocarbon of this group is produced, and only when dichromates are used is any appreciable amount of azo-derivative obtained. Only at first is there any difference in the behaviour of dichromates and chromates, as the former are soon converted into the latter by the alkaline hydroxide liberated. The actions are represented by the following equations:

$$K_2Cr_2O_7 + 3R{\cdot}NH{\cdot}NH_2 + H_2O = 2KOH + 2Cr(OH)_3 + 3RH + 3N_2,$$
$$2K_2CrO_4 + 3R{\cdot}NH{\cdot}NH_2 + 2H_2O = 4KOH + 2Cr(OH)_3 + 3RH + 3N_2.$$

With chromates, this simple reaction is the only one which occurs, and practically quantitative yields of hydrocarbon and nitrogen are obtained.

On adding a saturated solution of potassium dichromate to phenylhydrazine, a considerable rise of temperature takes place, nitrogen is rapidly evolved with much frothing, and benzene is formed. If the dichromate is in excess, potassium chromate and green chromium hydroxide are produced, whilst if excess of hydrazine is present a strongly alkaline liquid results containing hydrated chromium sesquioxide suspended in it.

Using excess of dichromate and carrying out the oxidation in a nitrometer, a yield of nitrogen amounting to about 92—95 per cent. of the theoretical was obtained. By distilling in steam, a similar percentage of the theoretical yield of benzene was collected, the loss being due mainly to the difficulty of condensing and separating the whole of the benzene from the water.

No diazo-compound could be detected among the products of the reaction, and only a minute quantity of a phenol-like substance could be extracted from the filtered alkaline residue after acidification. Only very small quantities of diphenyl and azobenzene were formed. The other hydrazines studied behaved similarly.

Potassium chromate alone or in presence of potassium hydroxide does not appreciably oxidise phenylhydrazine at the ordinary temperature. On heating nearly to boiling, oxidation commences, nitrogen is evolved, and benzene and a very little diphenyl are produced. The action goes on very quietly and regularly, and the yield of benzene and nitrogen is nearly quantitative. It is difficult, however, without special precautions, to retain the whole of the benzene, the vapour of which is carried away by the escaping nitrogen.

As a rule, in a carefully conducted experiment about 75 per cent. of the theoretical yield of pure dry benzene can be obtained. No tar, phenol, or diazo-compound is produced in this oxidation.

The quantitative nature of the reaction is shown better when *o*- or *p*-tolylhydrazine or *p*-bromophenylhydrazine is thus oxidised, since in these cases the loss of hydrocarbon or substituted hydrocarbon through volatilisation and imperfect condensation is not so great.

On account of the insolubility of *p*-bromophenylhydrazine in water, a saturated, aqueous solution of potassium chromate acts much less readily on it than on unsubstituted phenylhydrazine. Very little action occurs until the liquid boils, but oxidation then proceeds slowly and regularly without the formation of any tar, or of any recognisable quantity of by-products. Nitrogen and bromobenzene are produced in practically theoretical amount, the latter passing over and condensing with the steam; hydrated chromium sesquioxide separates, and the liquid becomes strongly alkaline from the liberation of potassium hydroxide.

Both the tolylhydrazines are similarly quantitatively oxidised by a hot saturated, aqueous solution of potassium chromate. Nitrogen, toluene, and a very little ditolyl are formed, and, as before, the chromate is reduced to hydrated chromium sesquioxide and potassium hydroxide.

The oxidation of aromatic hydrazines by potassium chromate is conveniently carried out by dissolving one and a-half times the amount of potassium chromate needed and its own weight of potassium hydroxide in about ten times its weight of water, and adding the hydrazine or its hydrochloride, using, in the latter case, correspondingly more potash. On blowing steam into the mixture, oxidation progresses quietly, the hydrocarbon condenses with the steam, and hydrated chromium sesquioxide separates from the liquid. In a carefully conducted experiment, a practically theoretical yield of hydrocarbon can be obtained.

The author desires to express his thanks to the Government Grant Committee of the Royal Society for a grant which has defrayed much of the cost of this investigation, and to Dr. H. B. Baker for so willingly placing the resources of the Christ Church Laboratory at his service.

CHRIST CHURCH,
OXFORD.

XXVI.—*The Reaction between Calcium Carbonate and Chlorine Water.*

By ARTHUR RICHARDSON, Ph.D.

IT is known that when chlorine is passed into water containing calcium carbonate in suspension, hypochlorous acid and calcium chloride are formed, carbon dioxide being given off, and that the hypochlorous acid can be separated from the calcium chloride by distillation. Williamson (*Mem. Chem. Soc.*, 1850, **2**, 234), who first observed this change, showed that in dilute solutions the reaction was represented by the equation:

$$CaCO_3 + 2Cl_2 + H_2O = CaCl_2 + 2HClO + CO_2.$$

He further showed that, when the amount of carbonate decomposed exceeded 1 part in 30 parts of water, the hypochlorous acid was partly replaced by calcium chlorate, the amount of the latter increasing with the weight of calcium carbonate decomposed.

Later experiments of the author (Trans., 1903, **83**, 380) have shown that hypochlorous and hydrochloric acids are formed in solutions of chlorine gas in pure water, provided that the two acids are at once separated by distillation; and it seemed probable that, in the presence of calcium carbonate also, if the two acids were first produced by the action of the chlorine on the water, the hydrochloric acid and the calcium carbonate would react to give calcium chloride and carbon dioxide, and the hypochlorous acid would be left free in the solution.

It will here be shown, however, that the reactions are not so simple as at first sight appears, for, in certain circumstances, a part of the hypochlorous acid is replaced by calcium hypochlorite, and the formation of calcium chlorate is accompanied by the liberation of oxygen.

The present experiments therefore were made for the further study of the action of chlorine water on calcium carbonate and the conditions under which these reactions occur.

The calcium carbonate used in these experiments was very carefully purified, especially from traces of iron and manganese; before using, it was dissolved in specially purified hydrochloric acid, reprecipitated with ammonium carbonate and kept at boiling point for several hours, and then finally washed entirely free from ammonium salts. This coarse granular precipitate was always used in preference to the carbonate in a more finely-divided condition.

The chlorine was prepared from potassium dichromate and hydrochloric acid, and was washed by passing it through solutions of chromic acid and then through water.

Estimation of Active Chlorine. ("Hypochlorous" Chlorine).—In all the following experiments, the chlorine was led into a measured volume of water containing known quantities of the calcium carbonate in suspension. Of course, at the end of an experiment there was excess of free chlorine in the solution. To give an idea of how the "hypochlorous" chlorine was determined, the details of an experiment are given: 10 c.c. of the solution (containing free and "hypochlorous" chlorine) were made up to 500 c.c. with water. This solution was divided into two equal parts, in one both the free and the "hypochlorous" chlorine were estimated together by means of potassium iodide, acidified with hydrochloric acid, and decinormal thiosulphate solution; in the other, the free chlorine was removed by aspirating a current of carbon dioxide for twenty-four hours; the residual hypochlorous acid was then estimated as before. Various experiments show that the free and the "hypochlorous" chlorine can be estimated with accuracy by this means, provided that the hypochlorous acid is not present in greater strength than about 0·0426 gram of hypochlorous acid in 100 c.c. of water. Moreover, the amount of free and "hypochlorous" chlorine was also checked by estimation with a *N*/10 solution of silver nitrate. The following table gives the results of three experiments:

TABLE I.

10 c.c. made up to 500 c.c. with water	I.	II.	III.
Free and "hypochlorous" chlorine	0·0884	0·0958	0·170
"Hypochlorous" chlorine	0·0643	0·0798	0·142
Free chlorine	0·0241	0·0160	0·028
Free and "hypochlorous" chlorine estimated by $AgNO_3$	0·0887	0·0958	0·170

It was necessary, also, to be able to determine the amount of chlorine present as calcium chloride (and also occasionally as calcium chlorate). This was done as follows: Hydrogen sulphide was passed through a cold solution containing the free chlorine, the "hypochlorous" chlorine, and the "calcium-chloride" chlorine (and sometimes "calcium-chlorate" chlorine). By this means, all the chlorine except the "chlorate" chlorine was converted into chloride, which could then be estimated with *N*/10 silver nitrate solution after the hydrogen sulphide had been expelled by boiling the solution. By subtracting from the total chlorine found the amount of free and "hypochlorous" chlorine, the amount of chlorine present as calcium chloride could be determined.

The amount of chlorine as chlorate was estimated by first determining the total chlorine as above, and also after an equal volume of the solution had been treated with Gladstone and Tribe's zinc-copper couple (as modified by Bothamley and Thompson, Trans., 1888, **53**, 164); the difference between these values gives the amount of chlorine present as chlorate.

Action of Chlorine on a Mixture of Calcium Carbonate and Water in the Cold.

When cold chlorine water is agitated with calcium carbonate, all free chlorine is at first removed, calcium chloride and hypochlorous acid alone being formed with evolution of carbon dioxide. But when the solution of hypochlorous acid becomes of more than a certain strength (about 4 per cent. HClO), it will be seen from the next table that chlorate begins to be formed; doubtless this is due to decomposition of the hypochlorous acid into hydrochloric and chloric acids:

TABLE II.

Expt.	Weight of $CaCO_3$ in 200 c.c. H_2O. Grams.	Ratio of $CaCO_3$ to H_2O.	"Hypochlorous" chlorine. In c.c.	"Chlorate" chlorine. In c.c.	"Chloride." chlorine. In c.c.
1	2	1 : 100	1·456	none	1·45
2	5	1 : 40	1·917	none	1·988
3	6	1 : 33·3	2·929	0·142	3·639
4	8	1 : 25	3·195	0·284	4·544
5	12	1 : 16·6	3·621	0·613	6·745
6	20	1 : 10	2·804	1·349	11·679

From this table, it will be seen that the "hypochlorous" chlorine* reaches a maximum in experiment 5, but that as the calcium chloride increases beyond this point the hypochlorous acid is less stable.

Also, it will be seen that in experiments 1 and 2, where no chlorate is formed, the amount of "hypochlorous" and "chloride" chlorine is the same; this can be expressed by the equation:

$$CaCO_3 + 2Cl_2 + H_2O = CaCl_2 + 2HClO + CO_2;$$

and if the formation of the chlorate is the only other reaction, then it may be expressed by the equation:

$$3HClO = HClO_3 + 2HCl.$$

That this second equation represents the only other reaction is not borne out by the results. This can be seen from the amount of "chloride" chlorine found. In experiment 3, 2·929 "hypochlorous" chlorine = 2·929 "chloride" chlorine, and 0·142 "chlorate" chlorine = 0·284 "chloride" chlorine, giving a total of 3·213 "chloride" chlorine, but 3·639 was the amount found. Again, in experiment 6, from the "hypochlorous" and "chlorate" chlorine there should be 5·502 "chloride" chlorine, but 11·679 was found.

---

* To avoid complication, it has been assumed that the "hypochlorous" chlorine is present entirely as hypochlorous acid; it will be shown later, however, that sometimes a part is present as the calcium salt.

The next set of experiments was made to determine whether calcium chloride had any influence on the reaction.

Influence of Calcium Chloride on the Action of Chlorine on a Mixture of Calcium Carbonate and Water in the Cold.

Two hundred c.c. of water containing 50 per cent. of calcium chloride in solution were treated with a small quantity of calcium carbonate and chlorine, the gas being passed into the mixture for two hours. The carbonate remained undissolved, and no trace of hypochlorous acid could be detected. Strong solutions of calcium chloride therefore entirely prevent the action of chlorine on calcium carbonate. When a 25 per cent. solution of calcium chloride was used, a limited action took place. Moreover, it was found that the solution (after getting rid of all free chlorine) gave a white, crystalline precipitate of calcium carbonate when treated with carbon dioxide. The original solution gave no such precipitate with carbon dioxide, therefore either calcium hydroxide or calcium hypochlorite had been formed during the reaction. Considering the amount of free chlorine present, it seemed unlikely that calcium hydroxide would be formed. It has been stated, however, by von Tiesenholt (*J. pr. Chem.*, 1901, [ii], **63**, 30) that anhydrous calcium chloride, to which a small quantity of a solution of hypochlorous acid has been added, becomes strongly alkaline, owing to the formation of calcium hydroxide. To determine whether this had taken place, a method based on the following considerations was adopted. If the calcium carbonate is formed from calcium hydroxide by the carbon dioxide, no additional hypochlorous acid will be liberated; if, however, it is formed from calcium hypochlorite, additional hypochlorous acid should be formed.

One hundred and fifty c.c. of a 6 per cent. solution of calcium chloride were treated with an excess of calcium carbonate, and chlorine passed for two hours. The solution was then filtered. Carbon dioxide was then passed through 50 c.c. of the solution, when a comparatively large amount of carbonate was precipitated, and the free chlorine was removed. Another 50 c.c. were aspirated by means of an air current to remove all free chlorine until the escaping gas, when bubbled through potassium iodide solution, scarcely gave a coloration of iodine; then carbon dioxide was substituted for air, and the current passed at as nearly as possible the same rate. The escaping gas was led into a solution of potassium iodide, and iodine was at once freely liberated. Thus air aspirated through the solution fails to liberate hypochlorous acid, but carbon dioxide passed through for the same time does. This fact seems to prove conclusively that calcium hypochlorite was present in the original solution.

A quantitative experiment was now made to determine the ratio of calcium hypochlorite to hypochlorous acid formed. One hundred c.c. of a 28 per cent. solution of calcium chloride were taken; to this, small quantities of calcium carbonate were added from time to time, and chlorine was passed through the mixture for four hours. Undecomposed calcium carbonate was then filtered off, and carbon dioxide passed through 50 c.c. of the solution until no more calcium carbonate was precipitated, and the free chlorine was removed. The solution was then boiled and filtered, and the precipitate was washed free of chloride and chlorate. The precipitate was converted into calcium oxalate, and the oxalic acid estimated by means of potassium permanganate; an amount was found equivalent to 0·2556 of "calcium hypochlorite" chlorine.

In another portion of the solution, the "hypochlorous" chlorine was estimated by the thiosulphate method. The amount was 0·248 of "hypochlorous" chlorine, thus showing that in the solution a little more than 50 per cent. of the "hypochlorous" chlorine was present as calcium hypochlorite.

Determination of the Amount of Calcium Hypochlorite Formed in the Absence of Added Calcium Chloride.

The following experiments were carried out in the manner already indicated; 6, 12, and 24 grams of calcium carbonate were added to 200 c.c. of water:

TABLE III.

Expt.	Weight of $CaCO_3$ in 200 c.c. water. Grams.	Ratio of $CaCO_3$ to water.	Chlorine as $Ca(ClO)_2$.	Total "hypochlorous acid" chlorine.	% of $Ca(ClO)_2$.
1	6	1 : 33·3	absent	5·857	0
2	12	1 : 16·6	0·361	7·224	5
3	24	1 : 8·3	0·761	5·609	15

Up to this point, the active chlorine was assumed to be present only as hypochlorous acid and hypochlorite; chlorous acid and its salts had not been looked for. To determine whether chlorous compounds were also present, a solution was prepared by decomposition of calcium carbonate in chlorine water, which gave a precipitate of calcium carbonate when treated with carbon dioxide. In one portion of the solution, the total active chlorine was estimated with sodium thiosulphate, and in another with an alkaline solution of arsenious oxide, using indigo as indicator. The two series of determinations agreed exactly, showing that chlorous acid or chlorites were absent. Hypochlorous and chlorous acids are both reduced by thiosulphates, but hypochlorous acid alone is capable of being decomposed by a solution of arsenious oxide. As all the foregoing experiments had been conducted in the cold, the influence of heat was now tried.

Influence of Heat on the Action of Chlorine on a Mixture of Calcium Carbonate and Water.

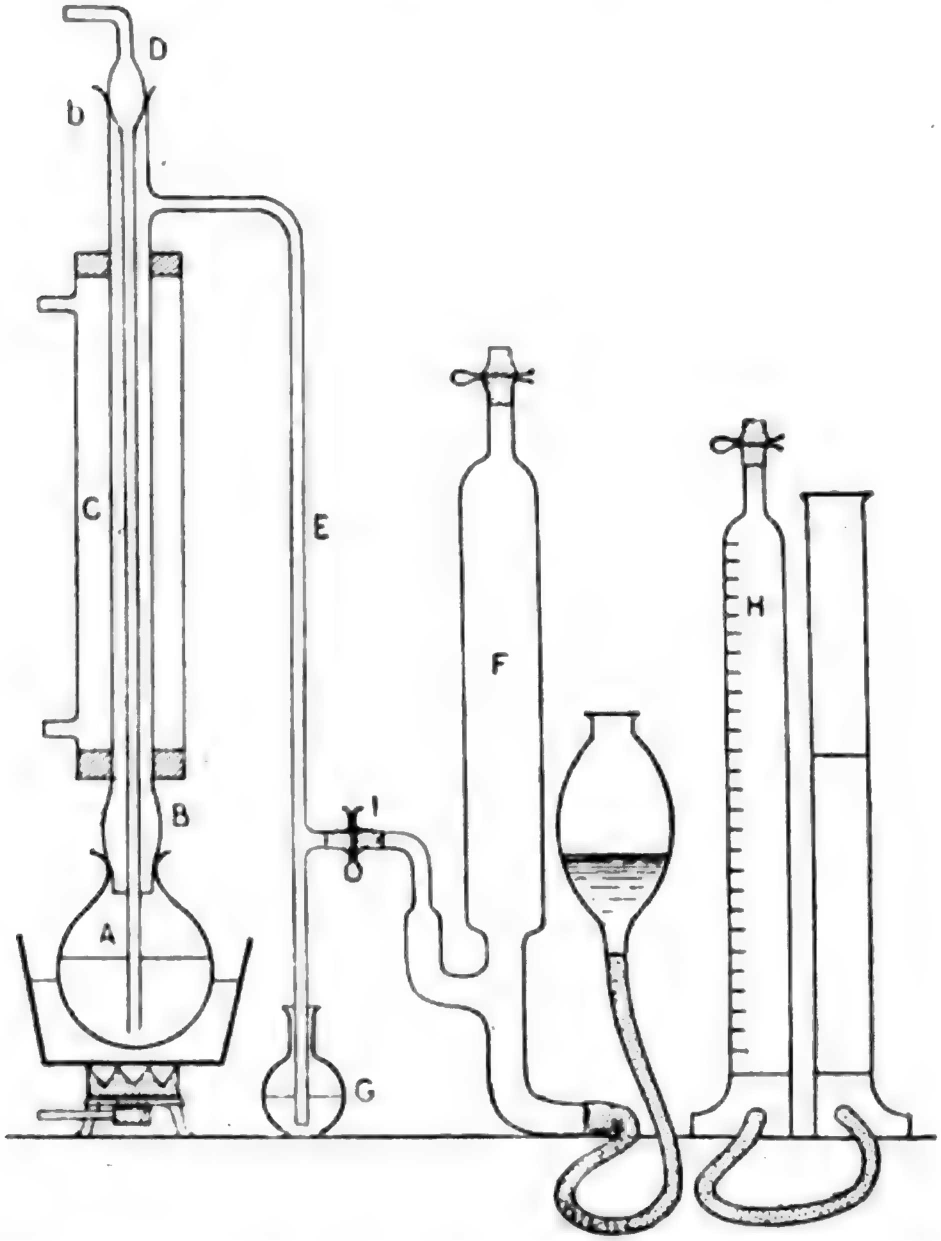
Referring back to table II, experiment 6, it will be seen that the amount of "chloride" chlorine (11·679) is in excess of what should have been produced (5·5) when calculated from the "hypochlorous" and "chlorate" chlorine. This can only be accounted for by oxygen being liberated during the reaction. In an early experiment, when the products of the action of chlorine on calcium carbonate and water were heated, oxygen was found to be formed. A special form of apparatus was therefore devised in order to make a series of quantitative determinations of the oxygen thus liberated (compare figure). The hypochlorous acid that remained after heating, the calcium chlorate, and the calcium chloride were also determined.

A spherical flask, *A*, was connected with the inner tube, *B*, of an upright Liebig's condenser, *C*, the neck of *A* and the lower end of *B* being ground into one another. A tube, *D*, passed down *B* to the bottom of *A* for the admission of chlorine, *D* being also ground into the upper part of *B*. The exit tube, *E*, sealed into the upper part of *B*, connected *A* with the gas-collecting tube, *F*, containing a strong solution of sodium hydroxide. Any gas passing from *A* and unabsorbed in *F* was measured in the gas burette, *H*.

Chlorine was first passed into cold water containing calcium carbonate in suspension in *A*, and, when all air had been removed from the apparatus (shown by complete absorption of the chlorine in a solution of sodium hydroxide in *G*), connexion was made between *F* and *A* by opening the stopcock at *I*. The flask, *A*, was then heated in an oil-bath. On heating, oxygen was at first freely evolved, but the rate of evolution rapidly diminished. In each experiment, the solution was heated for one and a-half hours, by which time no more oxygen was liberated. It will be seen that by this arrangement the hypochlorous acid formed would condense in *B* and return to *A*, where any change resulting from the action of hypochlorous acid on the other products would take place. In table IV, the results obtained are given:

TABLE IV.

Expt.	Weight of $CaCO_3$ in 300 c.c. water. Grams.	Ratio of $CaCO_3$ to water.	Oxygen found at N.T.P. In c.c.	"Hypochlorous acid" chlorine.	"Chlorate" chlorine.	"Chloride chlorine.
1	3	1 : 100	50·4	0·488	0·213	1·384
2	6	1 : 50	83·4	0·293	0·639	3·674
3	12	1 : 25	134	0·186	0·958	7·082
4	12	1 : 25	(a) 75·3* (b) 72·8	0·133	1·278	6·949



To determine whether the liberation of oxygen here observed was due to the action of heat on the hypochlorous acid in the absence of other compounds, the following experiments were made: (1) 200 c.c. of a solution of hypochlorous acid containing 2·059 grams of "hypochlorous" chlorine were heated for one and a-half hours in a stream of chlorine; 6 c.c. of oxygen were liberated, and the "hypochlorous" chlorine remaining was 1·153 grams; (2) 200 c.c. of a solution of hypochlorous acid containing 0·745 gram of "hypochlorous" chlorine were boiled for two hours, when 13 c.c. of oxygen were liberated and 0·639 gram of "hypochlorous" chlorine remained; but the remainder of this solution on again heating with some calcium carbonate yielded 54 c.c. of oxygen, and the "hypochlorous" chlorine had sunk to a value of 0·159 gram.

---

* In the first three experiments, the carbonate was completely decomposed in the cold solution, and then heated. In the fourth, a portion (about half) of the carbonate was decomposed and then heated, when 75·3 c.c. of oxygen were liberated; on cooling and repeating the experiment so as completely to dissolve the remaining carbonate, 72·8 c.c. more oxygen were produced.

Hypochlorous acid alone, therefore, when heated does not yield much free oxygen. Another experiment was made in which the "chlorate" and "chloride" chlorine was determined: a solution of hypochlorous acid containing 1·109 grams of "hypochlorous" chlorine was heated with some calcium carbonate; 41 c.c. of oxygen (at N.T.P.) were liberated, and 0·745 gram of "chloride" chlorine and 0·355 gram of "chlorate" chlorine were found. The amount of "chloride" chlorine found is more than double the "chlorate" chlorine, the extra amount being due to the oxygen liberated. The liberation of oxygen when a solution of hypochlorous acid is heated is most probably due to decomposition of chlorine monoxide: $2HClO = H_2O + O + Cl_2$. If this is so, then free chlorine should be produced as well as oxygen.

Instead of taking hypochlorous acid and calcium carbonate, calcium chloride was used. On warming a solution of hypochlorous acid and calcium chloride, a considerable amount of free chlorine was produced as well as oxygen. The formation of chlorate after treatment of hypochlorous acid with calcium chloride, and its absence in the original hypochlorous acid solution, was shown by dividing a solution of hypochlorous acid into equal volumes, one only being heated with a solution of calcium chloride. Both were then treated with hydrogen sulphide, boiled, and distilled with hydrochloric acid. The one containing calcium chloride gave chlorine and oxides of chlorine, which liberated iodine freely from potassium iodide, the other gave no such reaction.

Some further experiments were made to determine the ratio of the amount of chlorate formed and the oxygen liberated. A solution of hypochlorous acid containing 0·756 gram of "hypochlorous" chlorine and a strong solution of calcium chloride was decomposed by heat in an atmosphere of carbon dioxide; "chlorate" chlorine = 0·107 gram and oxygen liberated = 11·8 c.c. (at N.T.P.). *

In another experiment, a solution of hypochlorous acid containing 0·551 gram of "hypochlorous" chlorine and a strong solution of calcium chloride was similarly decomposed; "chlorate" chlorine = 0·089 gram and oxygen liberated = 12·2 c.c. (at N.T.P.).

---

* The atomic ratio calculated from these figures is roughly 3 atoms of chlorine to 1 atom of oxygen.

From the foregoing experiments, it will be seen that, in the first place, in mixtures of calcium carbonate and water in the cold where there is not a large excess of calcium carbonate, the reaction can be expressed as follows:

$$CaCO_3 + 2CO_2 + H_2O = CaCl_2 + 2HClO + CO_2.$$

When, however, the hypochlorous acid is above a certain strength, then a certain amount of calcium hypochlorite is formed, and also calcium chlorate and calcium chloride. As the amount of calcium chloride increases, the ratio of calcium hypochlorite to hypochlorous acid also increases. When chlorine is passed through a hot solution of calcium chloride with calcium carbonate in suspension, calcium chlorate, chloride, oxygen, and free chlorine are formed. In this case, hypochlorous acid appears to be the compound which is decomposed, yielding the free oxygen and chlorine.

CENTRAL HINDU COLLEGE,
BENARES, INDIA.

XXVII.—*Contributions to the Chemistry of the Terpenes. Part III. Some Oxidation Products of Pinene.*

By GEORGE GERALD HENDERSON and ISIDORE MORRIS HEILBRON.

THE additive compound $C_{10}H_{16},2CrO_2Cl_2$, which is formed by the action of chromyl chloride on pinene under suitable conditions (Henderson and Gray, Trans., 1903, **83**, 1299), yields when decomposed by water a saturated aldehyde, an unsaturated ketone, and a small quantity of a chlorinated oxidation product, together with much resinous matter. The aldehyde is easily converted into the corresponding acid, and, as it was found that a bromo-derivative of this could not be obtained by direct bromination, the *chloride*, $C_9H_{15}\cdot COCl$, was prepared from the acid. This chloride is a heavy, oily liquid, which reacts readily with water, and when heated with bromine under pressure is converted easily and completely into the *bromo*-derivative, $C_9H_{14}Br\cdot COCl$. This compound is very similar in properties to the chloride, and is decomposed by water with formation of the crystalline *bromo-acid*, $C_9H_{14}Br\cdot CO_2H$. When boiled with aqueous sodium carbonate, the bromo-acid is converted into the corresponding *hydroxy-acid*, $C_9H_{14}(OH)\cdot CO_2H$, which crystallises in needles and is soluble, although not readily, in water. Its *sodium* salt is readily, and its *silver* salt very sparingly, soluble in water.

When the impure bromo-acid, prepared by the action of water on its chloride, was treated with cold aqueous sodium carbonate, there remained undissolved a small quantity of a neutral compound which contains both bromine and oxygen. It crystallises from alcohol in small, colourless prisms, and appears to have the composition represented by the formula $C_{10}H_{13}OBr$.

The crude hydroxy-acid, precipitated by addition of dilute sulphuric acid to the alkaline solution obtained by heating the bromo-acid with sodium carbonate, was heated with water. The hydroxy-acid passed into solution, but a small quantity of another *acid* was left undissolved. This acid, of which the formula is probably $C_{10}H_{14}O_2$, crystallises from alcohol in silvery leaflets. Its *silver* salt crystallises from water in small, colourless needles.

The ketone described in the former paper on this subject (*loc. cit.*), to which the formula $C_{10}H_{14}O$ was provisionally assigned, has now been obtained in a purer state, and has been found to have the formula $C_9H_{14}O$. When reduced with sodium and alcohol, it yields the *alcohol*, $C_9H_{15}\cdot OH$, a viscous, colourless liquid, almost insoluble in water, but freely soluble in alcohol or ether. Its *phenylurethane* crystallises in delicate, colourless needles, and its *acid phthalic ester* in lustrous leaflets.

When heated with ammonium formate, the ketone is converted chiefly into the formyl derivative of an amine. The free *amine*, $C_9H_{15}\cdot NH_2$, is a colourless, oily liquid with a strong, disagreeable odour, and is almost insoluble in water. Its *hydrochloride* crystallises in silky needles which are extremely easily soluble in water, and its *platinichloride* is obtained in yellow leaflets.

The chlorinated oxidation product, separated from the ketone by repeated fractional distillations under diminished pressure, has the formula $C_{10}H_{15}OCl$. It crystallises from light petroleum in small prisms, and decomposes when heated above its melting point. It is very readily soluble in the usual organic solvents, and is not decomposed when heated with water. It does not yield an oxime or a semicarbazone, and when treated with sodium and alcohol it is slowly converted into a crystalline, strongly odorous compound which does not contain chlorine.

It is to be hoped that further investigation will throw light on the question of the constitution of the compounds described; in the meantime, it would hardly be profitable to indulge in speculation on the subject.

EXPERIMENTAL.

Preparation of the Hydroxy-Acid, $C_9H_{14}(OH)\cdot CO_2H$.

The calculated quantity of phosphorus pentachloride was mixed with light petroleum, and the dry, finely-powdered acid, $C_9H_{15}\cdot CO_2H$, was added in small quantities at a time. The mixture was left for some hours at the ordinary temperature and then heated on the water-bath under a reflux condenser until the action was completed. The light petroleum was evaporated, and the residue was then fractionally distilled under diminished pressure. The chloride of the acid was thus obtained in a purified state.

The *chloride*, $C_9H_{15}\cdot COCl$, is a colourless, somewhat viscous liquid, which boils at about 130° at 30 mm. pressure. It is denser than water and has a peculiar, but not unpleasant odour. It undergoes rapid decomposition when exposed to moist air, and is quickly converted into the corresponding acid by the action of cold water.

The *bromo*-derivative, $C_9H_{14}Br\cdot COCl$, was prepared by heating the chloride with a slight excess of bromine in a sealed tube at 100° for about twenty-four hours. This derivative is also a liquid, very similar in appearance to the chloride, and it reacts readily with water.

In order to prepare the corresponding acid, the bromo-derivative was poured into water, and the mixture was well stirred until all the oily compound was decomposed. The crystalline solid was collected, and treated with a cold aqueous solution of sodium carbonate. A small quantity of a solid which did not pass into solution was removed by filtration, the filtrate was acidified, and the bromo-acid which separated was purified by recrystallisation from dilute alcohol.

The *bromo-acid*, $C_9H_{14}Br\cdot CO_2H$, crystallises in small, colourless prisms. It is very readily soluble in alcohol or ether, and rather sparingly so in water.

The hydroxy-acid was obtained by boiling the bromo-acid with an aqueous solution of sodium carbonate for some hours under a reflux condenser. The solution was then concentrated, cooled, acidified with sulphuric acid, and shaken several times with ether. The ethereal solution was washed with water and dried with calcium chloride, the ether distilled off, and the residue was heated with water. Most of it passed into solution, but a small portion remained undissolved, and was separated by filtration; from the filtrate, on cooling, the hydroxy-acid separated in a crystalline state, and was purified by several crystallisations from water.

The *hydroxy-acid*, $C_9H_{14}(OH)\cdot CO_2H$, crystallises in small, colourless prisms, which melt at 227°. It is extremely easily soluble in alcohol, fairly so in water, and almost insoluble in light petroleum. When heated with insufficient water for solution, it melts and forms oily drops:

0·1884 gave 0·4486 CO_2 and 0·1520 H_2O. C = 64·9; H = 8·9.
0·1668 „ 0·3956 CO_2 „ 0·1305 H_2O. C = 64·8; H = 8·7.
$C_{10}H_{16}O_3$ requires C = 65·2; H = 8·7 per cent.

The *sodium* salt forms colourless crystals, which are readily soluble in water; the *silver* salt is obtained as a sparingly soluble, white, crystalline precipitate.

When boiled with lead peroxide and a little water, the hydroxy-acid does not yield a ketone, but is converted into the lead salt of another acid, of which the quantity available was too small to permit of examination.

The crystalline compound, which was produced along with the bromo-acid and was separated from the latter by its insolubility in cold aqueous sodium carbonate, was purified by crystallisation from alcohol. It crystallises in minute, colourless prisms, which melt at 173°, and is rather sparingly soluble in alcohol and insoluble in water. It is neutral in character, and on analysis it gave results which correspond fairly with those demanded by the formula $C_{10}H_{13}OBr$:

0·2476 gave 0·4710 CO_2 and 0·1332 H_2O. $C = 51·9$; $H = 6·0$.
0·1862 „ 0·1524 AgBr. $Br = 34·8$.
$C_{10}H_{13}OBr$ requires $C = 52·4$; $H = 5·7$; $Br = 34·9$ per cent.

Owing to the small quantity in our hands, we were not able to examine this compound more fully.

As stated above, another *acid* is formed in small quantity along with the hydroxy-acid when the bromo-acid is boiled with aqueous sodium carbonate. This acid was easily separated from the hydroxy-acid, as it is insoluble in water, and was purified by crystallisation from alcohol, in which it is rather sparingly soluble. It forms silvery leaflets, which melt at 144°, and it appears to have the composition $C_{10}H_{14}O_2$:

0·1200 gave 0·3164 CO_2 and 0·0956 H_2O. $C = 71·9$; $H = 8·8$.
$C_{10}H_{14}O_2$ requires $C = 72·3$; $H = 8·4$ per cent.

The *silver* salt of this acid crystallises from water, in which it is very sparingly soluble, in colourless needles:

0·0680 gave 0·0268 Ag. $Ag = 39·4$.
$C_{10}H_{13}O_2Ag$ requires $Ag = 39·6$ per cent.

The Ketone, $C_9H_{14}O$.

Owing to the difficulties met with in purifying the small quantity of the substance then at our disposal, the analyses of the ketone quoted in the first paper on this subject (*loc. cit.*), which pointed to the formula $C_{10}H_{14}O$, were open to suspicion, even although the determinations of the percentage of nitrogen in its semicarbazone also supported that formula. By the oxidation of fresh quantities of pinene, a larger supply of the ketone was obtained, and was first purified in the manner already described, and then repeatedly distilled, first under diminished and ultimately at atmospheric pressure, until a fraction of quite constant boiling point was separated. The pure ketone thus obtained boils at 209—210° under a pressure of 757 mm. A number of closely-agreeing analyses, of which two are quoted below, showed that the formula of the ketone is $C_9H_{14}O$:

0·1503 gave 0·4304 CO_2 and 0·1400 H_2O. C = 78·1 ; H = 10·3.
0·1612 „ 0·4608 CO_2 and 0·1528 H_2O. C = 78·0 ; H = 10·5.
$C_9H_{14}O$ requires C = 78·3 ; H = 10·1 per cent.

Determinations of the molecular weight of the ketone by the cryoscopic method gave similar results:

0·2350 in 30·32 acetic acid gave $\Delta t - 0·22°$. Mol. wt. = 136.
0·1635 „ 27·83 „ „ „ − 0·17°. „ = 134.
$C_9H_{14}O$ requires Mol. wt. = 138.

The semicarbazone of the ketone, it is true, was found to contain only 20·5 per cent. of nitrogen, whilst a semicarbazone of the formula $C_{10}H_{17}ON_3$ should contain 21·5 per cent. On the other hand, the analysis of the alcohol obtained by reduction of the ketone confirms the conclusion that the formula of the latter is $C_9H_{14}O$.

Preparation of the Alcohol, $C_9H_{15}\cdot OH$.

A solution of the ketone in alcohol was heated to boiling under a reflux condenser, and twice the theoretical quantity of sodium was gradually added. The liquid after cooling was mixed with water and almost completely neutralised with acetic acid, and the bulk of the alcohol was then distilled off. The residual liquid was shaken several times with ether, and the ethereal solution was washed with water and dried with anhydrous magnesium sulphate. After removal of the ether by distillation, the oily liquid which remained was fractionally distilled under diminished pressure; after several fractionations, the greater part distilled at a constant temperature.

The *alcohol*, $C_9H_{15}\cdot OH$, is a colourless, rather viscid liquid, with an odour somewhat like that of pinene. It boils at 147—148° under a pressure of 90 mm. It does not mix with water, but is freely soluble in alcohol or ether. It is unsaturated, uniting with two atomic proportions of bromine to form an additive compound, which, however, is unstable and quickly decomposes with evolution of hydrogen bromide:

0·3226 gave 0·9126 CO_2 and 0·3274 H_2O. C = 77·1 ; H = 11·4.
0·3660 „ 1·0362 CO_2 „ 0·3776 H_2O. C = 77·2 ; H = 11·5.
$C_9H_{16}O$ requires C = 77·1 ; H = 11·4 per cent.

The *phenylurethane*, $C_9H_{15}O\cdot CO\cdot NHPh$, was obtained by heating the alcohol with phenylcarbimide and recrystallising the product several times from dilute alcohol. It crystallises in colourless, lustrous prisms, which melt at 96°, and is very readily soluble in alcohol or ether, but insoluble in water:

0·2658 gave 13·2 c.c. nitrogen at 18° and 766 mm. N = 5·8.
$C_{16}H_{21}O_2N$ requires N = 5·4 per cent.

Several different methods of preparing a benzoate and an acetate from the alcohol were tried, but satisfactory products were not obtained. On the other hand, a crystalline *acid phthalic ester*, $CO_2H\cdot C_6H_4\cdot CO_2\cdot C_9H_{15}$, was easily produced. Equal weights of the alcohol and of finely-powdered phthalic anhydride were mixed with a little benzene and heated for some hours on the water-bath under a reflux condenser. The mixture was then poured into crushed ice, sodium carbonate was added in slight excess, and the insoluble portion removed by filtration. The filtrate was acidified with dilute sulphuric acid and shaken several times with ether. The ethereal solution was washed and dried, the ether removed by distillation, and the solid residue which remained was purified by several crystallisations from light petroleum.

The ester obtained in this way crystallises in silvery leaflets which melt at 107°. It is very readily soluble in alcohol or ether, sparingly so in light petroleum, and insoluble in water:

0·2398 gave 0·6246 CO_2 and 0·1598 H_2O. C = 70·9 ; H = 7·4.

$C_{17}H_{20}O_4$ requires C = 70·8 ; H = 6·9 per cent.

When treated with cold aqueous sodium carbonate, it passes readily into solution, forming a colourless *sodium* salt.

Preparation of the Amine, $C_9H_{15}\cdot NH_2$.

A mixture of the ketone with twice its weight of dry ammonium formate was heated in a sealed tube at 165° for twelve hours. After cooling, the contents of the tube were extracted with water and with ether, the ethereal solution was separated, evaporated, and the residue, which consisted for the most part of the formyl derivative of the amine, was hydrolysed by heating with an alcoholic solution of potassium hydroxide under a reflux condenser for about fifteen hours. After adding water to the solution, the amine was extracted by means of ether, and then removed from the ethereal solution by agitation with dilute hydrochloric acid. The solution of the hydrochloride was mixed with excess of potassium hydroxide, and the liberated amine was distilled in a current of steam and extracted from the distillate with ether. The ethereal solution was dried with potassium hydroxide, and then saturated with dry hydrogen chloride. The crystalline precipitate of the hydrochloride of the amine which separated was purified by solution in alcohol and precipitation with ether, and from the pure salt the amine was obtained by addition of potassium hydroxide and distillation with steam.

The *amine*, $C_9H_{15}\cdot NH_2$, is a colourless oily liquid with a strong disagreeable odour and an alkaline reaction. It is almost insoluble in water, but easily soluble in alcohol or ether, and it volatilises readily in steam. Unfortunately, the quantity of this compound obtained was too small to permit of the determination of its physical constants.

The *hydrochloride* of the amine, $C_9H_{15}\cdot NH_2,HCl$, crystallises in white, silky needles. It is extremely easily soluble in water or alcohol, but nearly insoluble in ether. On heating, it decomposes without melting, ammonium chloride being formed. The percentage of hydrogen chloride in the salt was determined, and the result agreed well with that required by the formula, although the quantity taken for analysis was of necessity very small.

The *platinichloride* of the amine, $(C_9H_{15}\cdot NH_2)_2,H_2PtCl_6$, crystallises in pale yellow leaflets, and is fairly readily soluble in water:

0·2438 gave 0·0702 Pt. Pt = 28·8.

$C_{18}H_{36}N_2Cl_6Pt$ requires Pt = 28·4 per cent.

Preparation of the Compound $C_{10}H_{15}OCl$.

The small quantities of a substance of higher boiling point, which were separated in the process of purifying several different preparations of the ketone, were mixed and subjected to fractional distillation under a pressure of 40 mm. in an atmosphere of dry carbon dioxide. The portion which distilled at 160—165° solidified on cooling to a pasty mass. From this product, the oily portion was separated as completely as possible by the aid of the pump, and the solid residue was drained on a porous plate, being then purified by several crystallisations from light petroleum. Further fractionations of the oily portion yielded an additional quantity of the crystalline compound.

The *compound* $C_{10}H_{15}OCl$ is a snow-white, crystalline solid with a slight odour. It melts at 168°, and when heated above its melting point at atmospheric pressure it is decomposed with formation of water, hydrogen chloride, and oily substances. Slight decomposition also occurs when it is heated under diminished pressure, similar decomposition products being formed in small quantity. It is insoluble in water, but very readily soluble in alcohol, ether, or light petroleum:

0·2074 gave 0·4932 CO_2 and 0·1508 H_2O. C = 64·7; H = 8·1.
0·2030 „ 0·1572 AgCl. Cl = 19·1.

$C_{10}H_{15}OCl$ requires C = 64·4; H = 8·0; Cl = 19·0 per cent.

It was found that this chlorinated oxidation product did not yield either an oxime or a semicarbazone, at least under usual conditions, and that it is very inert towards a number of other reagents. It is not decomposed by boiling water, and is scarcely affected when heated with moist silver oxide, or with silver acetate in presence of alcohol, or with a concentrated alcoholic solution of potassium hydroxide. However, it is slowly attacked by sodium ethoxide in hot alcoholic solution, and the following method of treatment was adopted. Sodium was added gradually to a concentrated alcoholic solution of the compound, which was then boiled under a reflux condenser for a considerable period. Sodium chloride slowly separated, and, when the reaction appeared to be at an end, water was added and the mixture was shaken several times with ether. The ethereal solution was separated, washed with water, and dried with calcium chloride, and after removal of the ether there remained a yellow, crystalline solid with a very strong odour like that of camphor. As this substance was found still to contain some chlorine, the treatment with sodium and alcohol was repeated several times. Finally, the product, separated as described, was purified by distillation in a current of steam and by crystallisation from dilute alcohol. In this way, a small quantity of a compound which contained no chlorine was obtained. It crystallises in small colourless prisms, which melt at about 165°, and has a very strong odour, somewhat like that of camphor. It is very readily soluble in the usual organic solvents, and it volatilises very easily in a current of steam. The quantity in our hands was insufficient for analysis.

We desire to express our thanks to the Committee of the Carnegie Trust for a grant which defrayed the expenses, and to Mr. James D. Fraser for assistance in part of the work.

CHEMISTRY DEPARTMENT,
THE GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

XXVIII.—*The Effect of Constitution on the Rotatory Power of Optically Active Ammonium Compounds. Part II.*

By HUMPHREY OWEN JONES and JOHN ROBERTSHAW HILL.

IN a former communication (Trans., 1906, **89**, 282) by Miss M. B. Thomas and one of us, the determination of the value of the rotatory powers of the ions of ten substituted ammonium compounds was described. These compounds formed two sets of five, all owing their activity to the presence of an asymmetric nitrogen atom attached to four alkyl groups; in one set, the phenyl, methyl, and benzyl groups were present together with one of the following alkyl groups: ethyl, *n*- or *iso*-propyl, *iso*butyl or *iso*amyl; in the other set of five compounds, the benzyl group was replaced by the allyl group.

The results obtained were discussed with reference to Guye's hypothesis as applied to the quinquevalent nitrogen atom, and it was decided that further experiments were necessary before deciding how far the hypothesis applied.

The present paper contains an account of the results obtained in the examination of a set of five substituted ammonium compounds containing the groups: *p*-bromophenyl, methyl, and allyl, together with one of the homologous groups, ethyl, *n*- or *iso*-propyl, *iso*butyl or *iso*amyl. This set therefore differs from the second set mentioned above by the introduction of a bromine atom into the phenyl group.

The substituted bromoanilines used were all new except one; their preparation and properties have already been described elsewhere by one of us (Hill, *Proc. Camb. Phil. Soc.*, 1907, **14**, 166), and it has also been shown (Hill, *ibid.*, 351) that the bromine atom had entered the benzene ring in the para-position with respect to the nitrogen atom.

The methods adopted for the resolution of the compounds and the mode of determining the rotatory power of the ion of the substituted ammonium salt has already been fully described in the former paper on this subject (*loc. cit.*).

p-*Bromophenylmethylethylallylammonium iodide* was deposited rapidly from a mixture of *p*-bromomethylethylaniline and allyl iodide in equimolecular proportions. After recrystallising repeatedly from alcohol, it formed colourless, stout prisms melting at 151°:

0·2248 gave 0·3100 CO_2 and 0·0900 H_2O. C = 37·6; H = 4·4.
$C_{12}H_{17}NBrI$ requires C = 37·7; H = 4·45 per cent.

p-*Bromophenylmethylethylallylammonium* d-*camphorsulphonate* was prepared in the usual way by mixing equivalent quantities of the substituted ammonium iodide and silver *d*-camphorsulphonate and boiling for some time with ethyl acetate and alcohol. After filtering and removing the solvent by evaporating on a water-bath, the residue was allowed to stand in a desiccator, when the *d*-camphorsulphonate readily crystallised. It was recrystallised repeatedly from acetone, and then melted at 153°.

After three recrystallisations, 0·2226 gram dissolved in 15·298 grams of water gave a rotation of 0·32°; hence $[M]_D$ +53·4°.*

After six recrystallisations, 0·2175 gram in 15·30 grams of water gave a rotation of 0·25°; hence $[M]_D$ +42·7°.

After nine recrystallisations, 0·2920 gram in 14·99 grams of water gave a rotation of 0·362°; hence $[M]_D$ +45·2°.

---

* All the determinations of rotatory power included in this paper were made in 2-dcm. tubes with a Landolt-Lippich triple field polarimeter, and, unless stated otherwise, the temperature was approximately 15°.

The iodide precipitated from this solution by the addition of potassium iodide gave a solution in alcohol which was inactive.

Thus the camphorsulphonate remains unresolved on recrystallisation from acetone.

It was afterwards recrystallised from amyl acetate at 100°. After three or four recrystallisations, 0·2154 gram dissolved in 15·54 grams of water gave a rotation of 0·28°; hence $[M]_D$ +49°.

Thus the rotatory power is not changed by recrystallising from amyl acetate at 100°.

p-*Bromophenylmethylethylallylammonium* d-*bromocamphorsulphonate* was prepared by the interaction of equimolecular proportions of silver *d*-bromocamphorsulphonate and the iodide in boiling acetone. The solution was filtered, evaporated on a water-bath, and allowed to stand in a vacuum desiccator, when it crystallised after some time. Attempts were made to recrystallise it from a large number of solvents and mixtures of solvents, but it invariably separated as an oil. It was next fractionally precipitated from acetone solution by the addition of light petroleum. This was done six times, but it still did not crystallise, and the iodide precipitated from a portion was found to be inactive.

The salt of Armstrong and Lowry's bromocamphorsulphonic acid was also prepared, but was not obtained crystalline.

Since it had been shown by Miss Homer (*Proc. Camb. Phil. Soc.*, 1907, **14**, 196) that asymmetric nitrogen compounds can be resolved by means of tartaric acid, it was decided to try this acid in this case.

p-*Bromophenylmethylethylallylammonium hydrogen* d-*tartrate* was therefore prepared in the following way. The iodide was dissolved in a mixture of alcohol and water, and slight excess of silver oxide added. After warming and allowing to stand for a short time, the solution was filtered from silver iodide, and an aqueous solution of the calculated quantity of *d*-tartaric acid was added. After evaporating the solution on a water-bath and allowing to stand in a desiccator, the tartrate crystallised. Some difficulty was experienced in finding a solvent from which the tartrate could be recrystallised, but eventually a mixture of alcohol and amyl acetate was found to answer the purpose. Afterwards, as purification of the tartrate proceeded, alcohol alone or a mixture of alcohol and ethyl acetate was used.

Analyses of the tartrate, dried over sulphuric acid in a desiccator, gave the following results:

0·2595 gave 0·4200 CO_2 and 0·1298 H_2O. C = 44·10; H = 5·5.

0·1968 „ 0·3190 CO_2 „ 0·1031 H_2O. C = 44·20; H = 5·82.

$C_{16}H_{22}O_6NBr$ requires C = 47·52; H = 5·45 per cent.

$C_{16}H_{22}O_6NBr,2H_2O$ requires C = 43·64; H = 5·91 per cent.

The tartrate melts at about 75° to a cloudy liquid, which effervesces at about 110° and becomes clear.

Thus it appears that the salt contains two molecules of water of crystallisation, the high results obtained for carbon probably being due to drying over sulphuric acid. It is remarkable that a salt should retain water of crystallisation in alcoholic solution, but other cases of the same kind have been observed by us and by others.

An attempt was made to estimate the percentage of water by heating the tartrate to 105°, but the weight decreased very slowly and continued to do so indefinitely, showing that decomposition takes place at this temperature.

After five recrystallisations, 0·2435 gram of tartrate, dissolved in 15·52 grams of water, gave $\alpha_D + 0{\cdot}21°$; hence $[\alpha]_D + 6{\cdot}4°$ and $[M]_D + 27°$.

After seven recrystallisations, 0·2024 gram in 15·30 grams of water gave $\alpha_D + 0{\cdot}13°$; hence $[\alpha]_D + 4{\cdot}9°$ and $[M]_D + 19{\cdot}8°$.

After ten recrystallisations, 0·2472 gram in 15·70 grams of water gave $\alpha_D + 0{\cdot}09°$; hence $[\alpha]_D + 2{\cdot}86°$ and $[M]_D + 11{\cdot}5°$.

After fourteen recrystallisations, 0·2467 gram in 15·31 grams of water gave $\alpha_D + 0{\cdot}09°$; hence $[\alpha]_D + 2{\cdot}8°$ and $[M]_D + 11{\cdot}3°$.

After seventeen recrystallisations, 0·2218 gram in 15·21 grams of water gave $\alpha_D + 0{\cdot}07°$ and $[M]_D + 9{\cdot}7°$.

Further recrystallisation did not seem to effect any measurable change.

The $[M]_D$ for $C_{16}H_{22}O_6NBr,2H_2O$, which corresponds with $[M]_D$ 10° for $C_{16}H_{22}O_6NBr$, is 10·9°.

Taking $[M]_D$ for the ion $C_4H_4O_6H$ as 42°, from the results of Landolt on ammonium hydrogen tartrate, we get $[M]_D$ for the ion $C_6H_4Br{\cdot}CH_3{\cdot}C_2H_5{\cdot}C_3H_5{\cdot}N-$ as about $-31°$.

The results on the whole are not very satisfactory, since the observed rotatory power is too small to enable us to determine whether the rotatory power is really constant, and a determination of the influence of temperature on the rotatory power is a hopeless task with such small readings. Attempts are being made to resolve this compound by means of other acids, in the hope of obtaining more satisfactory results.

The active iodide recovered from the tartrate melted at 142—143°, and was lævorotatory. So little of the iodide was obtained that trustworthy determinations of the rotatory power could not be made, but $[M]_D$ appears to be about $-20°$; $[M]_D$ for the same specimen in chloroform was $-26{\cdot}6°$, and autoracemisation occurred.

p-*Bromophenylmethyl*-n-*propylallylammonium iodide* was readily deposited in a crystalline state from a mixture of *p*-bromomethylethylaniline and allyl iodide in equimolecular proportions. The salt was readily recrystallised from alcohol, and separated in thin, colourless plates, usually hexagonal in shape, which melted at 140°:

0·2002 gave 0·2905 CO_2 and 0·0874 H_2O. C = 39·5; H = 4·85.

$C_{13}H_{19}NBrI$ requires C = 39·4; H = 4·80 per cent.

p-*Bromophenylmethyl*-n-*propylallylammonium* d-*camphorsulphonate* was prepared in the usual way, and was found to crystallise readily. When recrystallised repeatedly from either hot or cold ethyl acetate, it was found that the rotatory power of the salt in aqueous solution did not change appreciably, and did not differ much from that of the acid ion, as may be seen from the following determination:

0·3061 gram in 12·736 grams of solution gave $\alpha_D + 0·51°$; hence $[\alpha]_D + 10·6°$ and $[M]_D + 53·0°$.

The camphorsulphonate melts at 161—162°, but was not further examined, as the desired resolution was effected readily by means of the bromocamphorsulphonate.

p-*Bromophenylmethyl*-n-*propylallylammonium* d-*bromocamphorsulphonate* was prepared in the usual way, and was found to crystallise after standing for some time in a vacuum desiccator. The salt was crystallised at first from acetone and a little toluene, then, as its solubility in acetone diminished, acetone alone was used, and finally, in some cases only, acetone containing a trace of alcohol was used as solvent.

The melting point of the salt rose gradually, until it became constant at 159—160°, and the molecular rotatory power of the salt also increased and became constant at 416° after about three or four crystallisations. Analysis of the salt gave the following result:

0·2173 gave 0·3825 CO_2 and 0·1145 H_2O. C = 48·0; H = 5·85.

$C_{23}H_{33}O_4NBr_2S$ requires C = 47·8; H = 5·70 per cent.

Since the rotatory power of the basic ion in this salt proves to be less than that of the corresponding *iso*propyl ion, and in the corresponding phenyl series previously described (*loc. cit.*, p. 297) the rotatory powers of the *n*- and *iso*-propyl compounds were almost identical, special precautions were taken to see that the resolution was complete. The salt was resolved on three separate occasions, and cold and hot acetone with and without alcohol used as solvent, but in all cases the same result was obtained.

The following experiments suffice to prove that the separation is as complete as possible:

After three crystallisations, 0·1180 gram in 11·269 grams of solution gave $\alpha_D + 1·51°$; hence $[\alpha]_D + 72·1°$ and $[M]_D + 417°$.

After two further crystallisations from cold acetone, 0·1180 gram in 11·621 grams of solution gave $\alpha_D + 1·46°$; hence $[\alpha]_D + 71·9°$ and $[M]_D + 416°$.

After two further crystallisations from warm acetone, containing a trace of alcohol, 0·1581 gram in 11·235 grams of solution gave α_D +2·00°; hence $[\alpha]_D$ +71·0° and $[M]_D$ +412°.

These determinations and several others were carried out at the ordinary temperature of about 15°, and show that the molecular rotatory power of the salt may be taken as 416° at this temperature; taking that of the acid ion as 275°, the molecular rotatory power of the basic ion is obtained as 141°.

The influence of temperature on the rotatory power was then determined on a specimen of salt which gave a value of $[M]_D$ +417° at 15°.

0·1790 Gram in 16·022 grams of solution gave the following results (the salt is rather sparingly soluble in water, and this solution was practically saturated):

t.	α_D.	$[\alpha]_D$.	$[M]_D$.	$[M]_D$ for basic ion.
6°	1·62°	72·5°	420°	148°
12	1·61	72·0	417	143
25	1·60	71·6	414	134
45	1·56	70·6	409	120

The densities in all these dilute solutions are practically identical with those of water at the same temperature.

d-p-*Bromophenylmethyl*-n-*propylallylammonium iodide* was precipitated as colourless plates on the addition of a very concentrated potassium iodide solution to the saturated solution of the bromocamphorsulphonate. On account of the sparing solubility of the latter salt, only a small proportion of the iodide could be obtained.

The active iodide melts at 142—143°, whether taken as precipitated or after crystallising from cold alcohol.

Determinations of its rotatory power were made in solution in alcohol and in chloroform; the iodide is very sparingly soluble in the latter solvent, so that good values could not be obtained. The active iodide, like all those hitherto examined, undergoes autoracemisation in chloroform.

In ethyl alcohol at 15°:

0·118 gram in 9·377 grams of solution gave α_D +0·73° (density = 0·810); hence $[\alpha]_D$ +35·8° and $[M]_D$ +142°.

0·122 gram in 9·661 grams of solution gave α_D +0·76° (density = 0·811); hence $[\alpha]_D$ +37·1° and $[M]_D$ +147°.

0·118 gram in 9·270 grams of solution gave α_D +0·75° (density = 0·810); hence $[\alpha]_D$ +36·4° and $[M]_D$ +144°.

The value of the molecular rotatory power in ethyl alcohol may therefore be taken as 144°.

In chloroform :

0·0781 gram in 16·85 grams of solution gave a_D +0·80° (density = 1·494) ; hence $[a]_D$ +57·9° and $[M]_D$ +229°.

0·1080 gram in 16·532 grams of solution gave a_D +1·10° (density = 1·500) ; hence $[a]_D$ +56·2° and $[M]_D$ +222°.

Hence we may take the value of $[M]_D$ to be about 226° in chloroform, a value rather unusually large compared with that obtained in alcohol.

The rotatory power of these chloroform solutions fell to about three-fourths value in four hours, nine-sixteenths in nine hours, and became almost inactive in about forty-eight hours and quite inactive between forty-eight and seventy-two hours.

p-*Bromophenylmethyl*iso*propylallylammonium iodide*.—A mixture of the calculated quantities of *p*-bromomethyl*iso*propylaniline and allyl iodide gradually deposited crystals of the quaternary iodide on standing. After recrystallising several times from alcohol, the salt formed colourless, rectangular prisms or rhombs, melting at 153° :

0·2142 gave 0·3075 CO_2 and 0·0978 H_2O. C = 39·15 ; H = 5·07.

$C_{13}H_{19}NBrI$ requires C = 39·4 ; H = 4·80 per cent.

p-*Bromophenylmethyl*iso*propylallylammonium* d-*camphorsulphonate* was prepared by heating together calculated quantities of the iodide and silver *d*-camphorsulphonate with moist acetone. After filtering off the silver iodide, the acetone was evaporated, and the salt crystallised readily on standing a very short time. The camphorsulphonate was first recrystallised a few times from a mixture of acetone and toluene, then from acetone alone, and finally, as it became less soluble, from acetone and water.

After nine recrystallisations, 0·2248 gram of the salt in 15·4 grams solution gave a_D −0·01° ; hence $[M]_D$ −1·7°.

After twelve recrystallisations, 0·2560 gram in 16·46 grams of solution gave a_D −0·02° ; hence $[M]_D$ −3·2°.

After four more recrystallisations, 0·2272 gram in 15·28 grams of solution gave a_D −0·11° ; hence $[M]_D$ −18·5°.

Thus it appeared that the *lBdA* salt was being isolated, but the rotatory power was not yet constant, and it was clear that large quantities of the salt would have to be worked up. The salt melted at 163° :

0·1760 gave 0·3572 CO_2 and 0·1087 H_2O. C = 55·35 ; H = 6·86.

$C_{23}H_{34}O_4NBrS$ requires C = 55·20 ; H = 6·8 per cent.

Some time later, another attempt was made to resolve this salt. The salt from the mother liquors together with same freshly-prepared salt was recrystallised from acetone and a few drops of alcohol, as it was so sparingly soluble in acetone alone. The salt was now found to be strongly dextrorotatory, and it therefore appeared that the *dBdA* salt was being obtained.

After six recrystallisations, 0·2206 gram in 14·83 grams of water gave a_D +1·28°; hence $[M]_D$ +215·2°.

After eight recrystallisations, 0·2472 gram in 14·85 grams of water gave a_D +1·41°; hence $[M]_D$ +212°.

After ten recrystallisations, 0·1977 gram in 14·88 grams of water gave a_D +1·13°; hence $[M]_D$ +212·7°.

Thus it appears that the molecular rotatory power becomes constant at about 213°. This gives the value of $[M]_D$ for the basic ion as 161°.

We have not yet been able to find the explanation of these curious observations, and have not been able on subsequent occasions to isolate the *lBdA* salt; the *dBdA* salt when recrystallised from acetone and water did not become lævorotatory. The rotatory power of the *dBdA* salt was observed at different temperatures.

0·2395 Gram dissolved in 16·085 grams of water gave the following rotations (density = 1·002 at 15°):

t.	a_D.	$[a]_D$.	$[M]_D$.	$[M]_D$ for basic ion.
3°	1·30°	43·5°	217·5°	169·5°
10	1·28	42·9	215·0	165·5
20	1·25	41·9	210·0	158·5
30	1·22	40·9	205 0	151·4
40	1·20	40·2	203·0	147·4
50	1·18	39·5	200·0	142·4

The corresponding *d*-bromocamphorsulphonate was prepared, but did not crystallise.

d-*Bromophenylmethyl*iso*propylallylammonium iodide* was readily precipitated from an aqueous solution of the resolved camphorsulphonate by addition of concentrated potassium iodide solution. It melts at 153°, the same temperature as the inactive iodide.

The following determinations of its rotatory power in ethyl-alcoholic solution were made at 15°:

0·1154 gram in 12·69 grams of alcohol gave a_D +0·60° (density = 0·810); hence $[a]_D$ +40·7° and $[M]_D$ +165°.

0·2073 gram in 22·72 grams of alcohol gave a_D +0·59° (density = 0·81); hence $[a]_D$ +39·9° and $[M]_D$ +162°.

This iodide was very sparingly soluble in chloroform, and it was therefore not found possible to determine the rotatory power in this solvent.

p-*Bromophenylmethylisobutylallylammonium iodide* was deposited very slowly on mixing *p*-bromomethyl*iso*butylaniline with allyl iodide in equimolecular proportions. This salt was very soluble in alcohol, and crystallised with difficulty. It was recrystallised from acetone or from alcohol and ether, when it separated as microscopic prisms, melting at 135—136°:

0·2485 gave 0·3745 CO_2 and 0·1207 H_2O. C = 41·10; H = 5·39.
$C_{14}H_{21}NBrI$ requires C = 40·97; H = 5·12 per cent.

The d-*camphorsulphonate* was prepared and recrystallised repeatedly from acetone and light petroleum, but its molecular rotatory power was then found to be only just above 60°; further examination of this salt was abandoned, as the desired result was obtained by means of the bromocamphorsulphonate.

p-*Bromophenylmethylisobutylallylammonium* d-*bromocamphorsulphonate* was prepared by heating together the calculated quantities of silver *d*-bromocamphorsulphonate and the iodide in moist acetone. It crystallised readily from the filtrate after evaporating on a water-bath. It was recrystallised from acetone, in which it is readily soluble, or from acetone and light petroleum; the bromocamphorsulphonate melts at 138°:

0·2110 gave 0·3750 CO_2 and 0·1145 H_2O. C = 48·5; H = 6·03.
$C_{24}H_{35}O_4NBr_2S$ requires C = 48·6; H = 5·91 per cent.

The rotatory power of the salt gradually increased on recrystallisation, showing that the *dBdA* salt was being obtained. It was found very difficult to obtain a constant rotatory power, and several attempts had to be made, in which large quantities of the salt were used and the salt in the mother liquors was carefully worked up.

After about twenty-five recrystallisations, 0·1044 gram in 11·045 grams of water gave α_D + 1·16° (density = 1·001); hence $[\alpha]_D$ + 61·3° and $[M]_D$ + 364°.

After two more recrystallisations from acetone and light petroleum, 0·1027 gram in 11·007 grams of water gave α_D + 1·15°; hence $[\alpha]_D$ + 61·6° and $[M]_D$ + 366°.

After three more recrystallisations:

0·1250 gram in 11·37 grams of water gave α_D + 1·36°; hence $[\alpha]_D$ + 61·8° and $[M]_D$ + 366°.

0·1996 gram in 11·145 grams of water gave α_D + 2·25°; hence $[\alpha]_D$ + 62·8° and $[M]_D$ + 372°.

0·1198 gram in 11·42 grams of water gave α_D + 1·32°; hence $[\alpha]_D$ + 62·9° and $[M]_D$ + 373°.

Thus $[M]_D$ for the salt is 370° and for the basic ion is 95°.

The influence of temperature on the rotatory power of the salt was almost negligible, hence the following values may be taken for the molecular rotatory power of the ion: 103° at 0°, 95° at 15°, 86° at 30°, and 76° at 50°. These values are almost identical with those obtained for the corresponding *iso*amyl ion.

d-*Bromophenylmethylisobutylallylammonium iodide* was readily precipitated from an aqueous solution of the bromocamphorsulphonate of constant rotatory power by the addition of concentrated potassium iodide solution. It melts at 133—134°, and separates from alcohol in small prisms.

The following determinations of the rotatory power in alcohol were made at about 15°:

0·1515 gram in 12·71 grams of alcohol gave a_D $+0·53°$ (density = 0·810); hence $[a]_D$ $+27·4°$ and $[M]_D$ $+112°$.

After recrystallising from cold alcohol:

0·160 gram in 9·587 grams of solution gave a_D $+0·77°$ (density = 0·815); hence $[a]_D$ $+28·3°$ and $[M]_D$ $+116°$.

0·1501 gram in 9·687 grams of solution gave a_D $+0·73°$ (density = 0·816); hence $[a]_D$ $+28·9°$ and $[M]_D$ $+118°$.

The value of $[M]_D$ for the iodide in ethyl-alcoholic solution may therefore be taken as about 117°.

The active iodide is so sparingly soluble in chloroform that no trustworthy determinations of the rotatory power could be made. The following experiment, however, seems to show that the iodide has a greater rotatory power in chloroform than in alcohol, and that it undergoes autoracemisation:

0·029 gram in 17·916 grams of solution (practically saturated) gave a_D $+0·23°$ (density $= 1·490$); hence $[a]_D$ $+47·7°$ and $[M]_D$ $+195°$.

After four hours, a_D was 0·16°, and after forty-eight hours the solution was inactive.

p-*Bromophenylmethyl*iso*amylallylammonium iodide* was prepared from the tertiary amine and allyl iodide. It was somewhat soluble in alcohol, and was therefore recrystallised from a mixture of alcohol and ether, from which it separated in sheaf-like aggregates of long, colourless prisms, melting at 127—128°:

0·2962 gave 0·4581 CO_2 and 0·1435 H_2O. C = 42·2; H = 5·38.
$C_{15}H_{23}NBrI$ requires C = 42·4; H = 5·42 per cent.

The corresponding *bromide* was also prepared by the union of the amine and allyl bromide and recrystallised from alcohol and ether, when it formed colourless prisms melting at 161—162°:

0·2891 gave 0·5075 CO_2 and 0·1615 H_2O. C = 47·9; H = 6·21.
$C_{15}H_{23}NBr_2$ requires C = 47·8; H = 6·10 per cent.

p-*Bromophenylmethyl*iso*amylallylammonium* d-*camphorsulphonate* was prepared by boiling together equivalent quantities of the bromide or iodide and silver *d*-camphorsulphonate with moist acetone. The salt did not crystallise well, and after recrystallising several times from a mixture of acetone and toluene it was still somewhat viscid and melted at 65°.

From the following determination of its rotatory power, it is clear that resolution does not take place rapidly, if at all:

0·2000 gram in 12·83 grams of solution gave α_D +0·26°; hence $[M]_D$ +44°.

The bromocamphorsulphonate was therefore made, and it was found that this could be resolved more easily.

p-*Bromophenylmethylisoamylallylammonium* d-*bromocamphorsulphonate* was prepared in the usual way, using moist acetone as solvent; it crystallised readily, and could be recrystallised from acetone. After repeated recrystallisation from acetone, the salt formed stellate aggregates of needles and melted sharply at 170°:

0·2550 gave 0·4641 CO_2 and 0·1378 H_2O. C = 49·6; H = 6·00.

$C_{25}H_{37}O_4NBr_2S$ requires C = 49·4; H = 6·10 per cent.

It was found that the molecular rotatory power of the salt increased to about 360° after three or four recrystallisations from ethyl acetate or acetone, and further recrystallisation only served to raise the rotatory power to 370°. As this value is very close to that found for the *iso*butyl compound, the salt was repeatedly recrystallised both from hot and cold acetone and from cold ethyl acetate, and examined in order to make certain that resolution was complete and the rotatory power constant.

After six recrystallisations from warm acetone:

0·1330 gram in 11·600 grams of solution gave α_D +1·39° (density = 1·001); hence $[\alpha]_D$ +60·6° and $[M]_D$ +368°.

After two further recrystallisations from cold acetone:

0·121 gram in 11·934 grams of solution gave α_D +1·32° (density = 1·001); hence $[\alpha]_D$ +60·1° and $[M]_D$ +365°.

After two further recrystallisations from warm acetone:

0·1611 gram in 11·332 grams of solution gave α_D +1·74° (density = 1·002); hence $[\alpha]_D$ +61·1° and $[M]_D$ +371°.

The salt was now recrystallised from ethyl acetate, and successive fractions examined:

0·104 gram in 11·807 grams of solution gave α_D +1·08° (density = 1·000); hence $[\alpha]_D$ +61·1° and $[M]_D$ +371°.

0·1019 gram in 11·604 grams of solution gave α_D +1·07° (density = 1·000); hence $[\alpha]_D$ +60·8° and $[M]_D$ +369°.

It is clear that the salt was as pure as recrystallisation could make it; hence the molecular rotatory power may be taken as 369° at 16°, and $[M]_D$ for the basic ion is therefore 94°.

The following results were obtained in determining the influence of temperature on the rotatory power of the salt.

0·1829 gram in 15·845 grams of solution (density at 15° = 1·002):

t.	α_D.	$[\alpha]_D$.	$[M]_D$.	$[M]_D$ for basic ion.
10°	1·42°	61·4°	372°	99°
22	1·41	61·0	370	92
35	1·40	60·6	368	84
50	1·38	60·3	366	75

d-*Bromophenylmethylisoamylallylammonium iodide*.—When a concentrated solution of potassium iodide was added to a solution of the bromocamphorsulphonate, the solution became turbid and oily drops separated; on standing these became crystalline. The colourless crystals of the iodide when dried melted at 130—131°, and after crystallising from cold alcohol formed colourless prisms melting at 131—131·5°.

The rotatory power was determined in alcohol and in chloroform at about 15°. In alcohol:

0·124 gram in 8·702 grams of solution gave $\alpha_D + 0·60°$ (density = 0·810); hence $[\alpha]_D + 26·3°$ and $[M]_D + 111°$.

0·112 gram in 9·220 grams of solution gave $\alpha_D + 0·49°$ (density = 0·809); hence $[\alpha]_D + 25·2°$ and $[M]_D + 107°$.

0·1221 gram in 9·468 grams of solution gave $\alpha_D = 0·55°$ (density = 0·814); hence $[\alpha]_D + 26·2°$ and $[M]_D + 111°$.

0·1409 gram in 9·347 grams of solution gave $[\alpha]_D + 0·64°$ (density = 0·81); hence $[\alpha]_D + 26·2°$ and $[M]_D + 111°$.

Therefore the molecular rotatory power of the iodide may be taken as 111°.

In chloroform:

0·121 gram in 16·610 grams of solution gave $[\alpha]_D + 0·87°$ (density = 1·495); hence $[\alpha]_D + 39·9°$ and $[M]_D + 169°$.

After two and a-half hours, $\alpha_D + 0·78°$; after twenty-two hours, $\alpha_D + 0·15°$, and after forty-eight hours the solution was inactive.

The following table, containing the melting points and rotatory powers of the compounds described in this paper, is given for convenience of reference:

p-*Bromophenyl-methyl-allyl Series.*

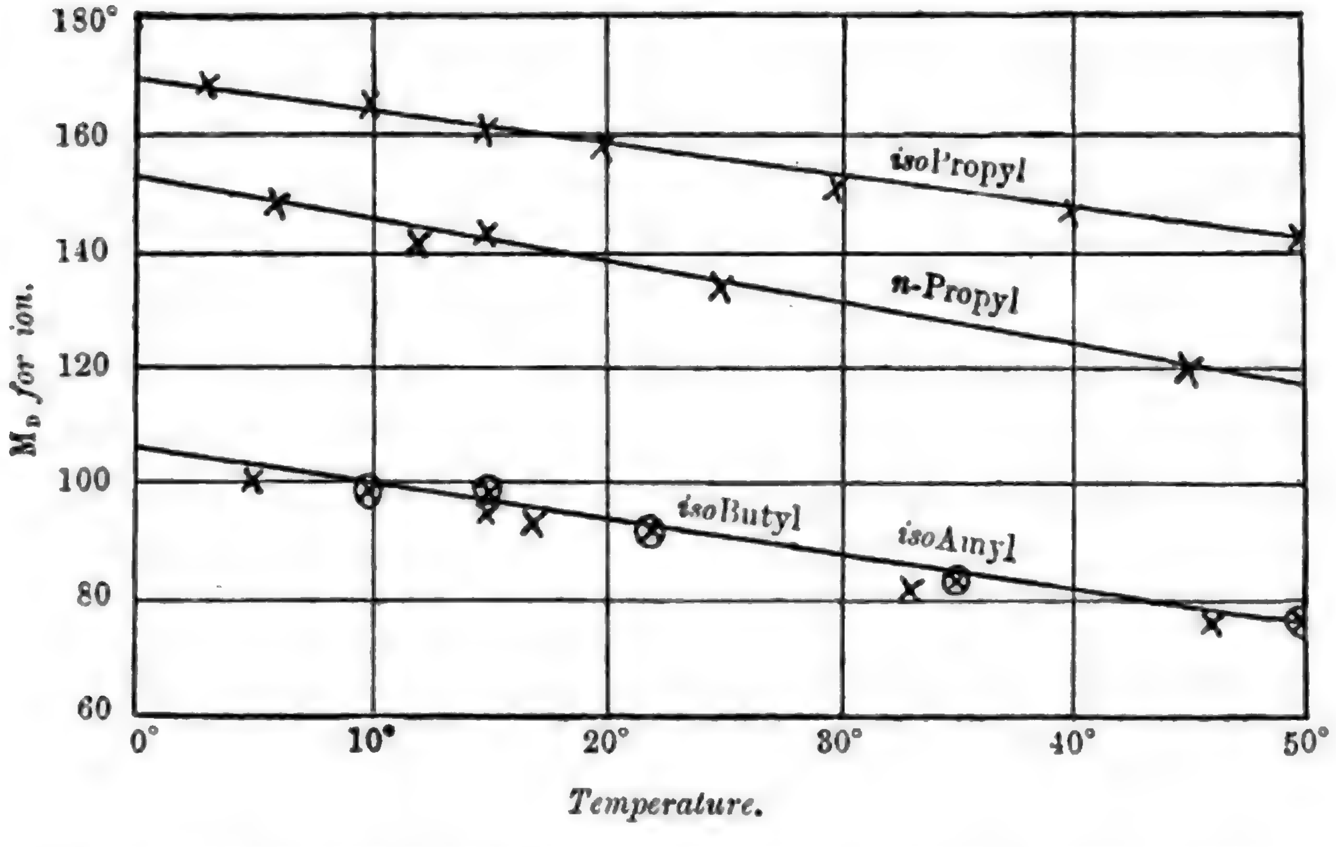
	M. p. of active iodide.	M. p. of *d*-camphor-sulphonate.	M. p. of *d*-bromo-camphor-sulphonate.	$[M]_D$ of ion at 15°.	$[M]_D$ of iodide in alcohol.	$[M]_D$ of iodide in chloroform.
Ethyl	151°	153°	—	−31° (?)	−20° (?)	−26° (?)
n-Propyl ...	142—143	161—162	159—160°	141	144	222
*iso*Propyl ...	153	163	—	151	165	—
*iso*Butyl ...	133—134	—	138	96	117	195
*iso*Amyl ...	135—136	65 (?)	170	94	111	169

The great similarity in the melting points of several of the compounds is as marked as in the corresponding set of phenyl compounds.

It will be seen from the table that the value of $[M]_D$ for the iodide in alcohol is in each case greater than that of the basic ion in water, and that the value of $[M]_D$ of the iodide is greater in chloroform solution than in alcohol. The latter statement is also true for all the active iodides examined in the former communication on this subject (*loc. cit.*, p. 304), and the first-mentioned relation is also true with one exception for the compounds then examined.

The following diagram shows that the influence of temperature on the rotatory powers of the ions is uniform throughout the range examined and of the same kind in all five cases.

FIG. 1.



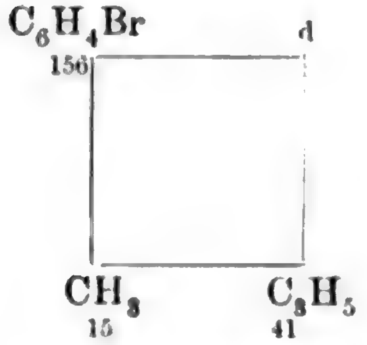
In the case of the *iso*butyl and *iso*amyl compounds, the points marked ⊕ refer to the *iso*butyl compound.

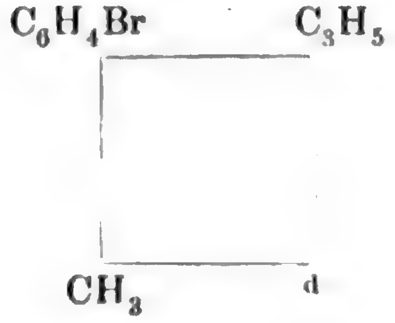
The relation between the values of the molecular rotatory powers of the ions and the values of the product of asymmetry for the asymmetric nitrogen atom or ion may now be discussed.

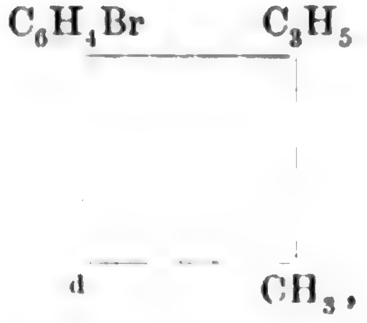
The formula for the product of asymmetry, p'', in terms of the masses of the four allyl groups developed in the former communication (*loc. cit.*, p. 308):

$$p'' = \frac{\{(a+d)-(b+c)\}\{(a+b)-(c+d)\}(a-c)(b-d)}{(a+b+c+d)^4}$$

applied to the three possible configurations for this series of compounds:







where *d* represents the group which is varied, gives the values for *p″* given in the following table, which also contains the values of $[M]_D$ for the basic ions at 15°.

p-*Bromophenyl-methyl-allyl Series.*

	[M] for basic ion.	I. $p'' \times 10^3$.	II. $p'' \times 10^3$.	III. $p'' \times 10^3$.
Ethyl	31°	6·22	15·1	9·9
n-Propyl	141	9·48	8·4	1·3
*iso*Propyl	161			
*iso*Butyl	96	10·6	4·5	8·4
*iso*Amyl	94	10·1	2·26	12·5

It is clear that there is no simple relation between the values of *p″* and $[M]_D$ even if, for the present, the somewhat doubtful values for the ethyl compound were neglected, and in this case no connexion can be seen even if the different compounds be assumed to possess different configurations.

The data given for the *iso*butyl and *iso*amyl compounds leave some slight doubt as to which ion has the greater rotatory power. Taking into consideration the fact that the iodide of the *iso*butyl compound has the greater rotatory power, it seems very probable that the basic ion also has a greater rotatory power than the corresponding ion containing the *iso*amyl group, especially as the evidence of complete resolution is more conclusive in the latter case.

The similarity of the rotatory powers of the *iso*butyl and *iso*amyl compounds is remarkable, and would seem to suggest that they have configuration I, but then the value of *p″* is greater than that for the propyl compounds. It is interesting to note also that, although in the phenyl-methyl-allyl series the rotatory powers of the *n*-propyl and *iso*propyl compounds were found to be almost identical, in this series the *n*- and *iso*-propyl compounds differ in the same way as they do in the phenyl-methyl-benzyl series, where the values of $[M]_D$ for the ions were found to be 299° and 398° respectively.

A similar case in which the *iso*propyl compound has a greater rotatory power than the *n*-propyl compound has recently been found by Piutti and Magli in the alkyl hydrogen aspartates (*Gazzetta*, 1906, **36**, ii, 738).

The series of compounds derived from the same substituted *p*-bromoanilines, but containing the benzyl instead of the allyl group, is also under examination, and the results of the examination of these and other active nitrogen compounds will be communicated to the Society later.

The expenses of this investigation have been defrayed by grants placed at our disposal by the Government Grant Committee of the Royal Society, for which we are glad to make this grateful acknowledgment.

University Chemical Laboratory,
Cambridge.

XXIX.—*The Preparation of* l-*Benzoin.*

By Alex. McKenzie and Henry Wren.

Although benzoin, $C_6H_5 \cdot CH(OH) \cdot CO \cdot C_6H_5$, contains an asymmetric carbon atom, it has not hitherto been obtained in an optically active form. Indeed, with the exception of *dl*-fructose, no externally compensated keto-alcohol has, so far as we know, been resolved into its optically active components by any of the ordinary methods.

In the present paper, the conversion of *l*-mandelic acid into *l*-benzoin is described.

Béis (*Compt. rend.*, 1903, **137**, 575) showed that ketones may be obtained from acid amides by aid of the Grignard reaction. When one molecular proportion of an acid amide is heated for several hours at the temperature of a boiling-water bath with more than two molecular proportions of a Grignard reagent, and the resulting compound then decomposed by ice and mineral acid in the usual manner, ketones are produced in yields varying from 20 to 50 per cent. The acid amides investigated by Béis from this standpoint were acetamide, propionamide, butyramide, *iso*valeramide, and benzamide, and the following ketones were isolated, methyl ethyl ketone, diethyl ketone, methyl propyl ketone, ethyl *iso*butyl ketone, acetophenone, and phenyl ethyl ketone.

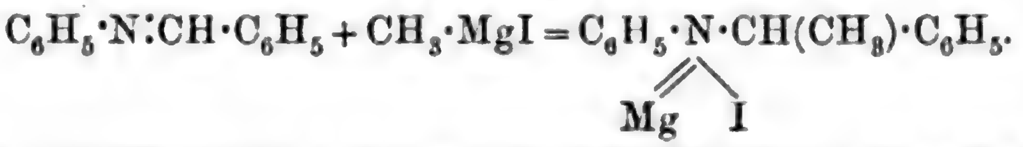
After we had applied this action of Béis to *r*-mandelamide and obtained ordinary benzoin by means of magnesium phenyl iodide or bromide, the behaviour of *l*-mandelamide was studied. *l*-Benzoin was isolated in this manner; it melts at 131—132·5°, reduces Fehling's solution, and has $[\alpha]_D^{10·5}$ $-118·6°$ for $c = 0·9232$ in acetone solution. Its formation may be represented by the following equations:

$$(1)\ C_6H_5{\cdot}CH(OH){\cdot}C(OH){:}NH + 3C_6H_5{\cdot}MgBr = C_6H_5{\cdot}CH(O{\cdot}MgBr){\cdot}C(O{\cdot}MgBr)(C_6H_5){\cdot}NH{\cdot}MgBr + 2C_6H_6.$$

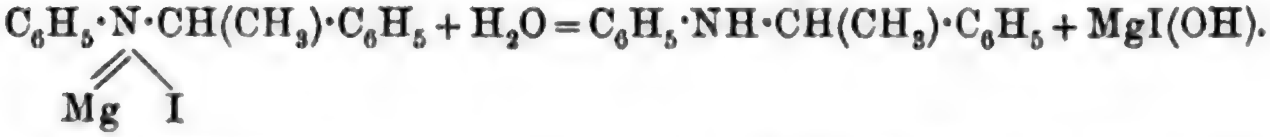
$$(2)\ C_6H_5{\cdot}CH(O{\cdot}MgBr){\cdot}C(O{\cdot}MgBr)(C_6H_5){\cdot}NH{\cdot}MgBr + 3H_2O = C_6H_5{\cdot}CH(OH){\cdot}C(OH)(C_6H_5){\cdot}NH_2 + 3MgBr(OH).$$

$$(3)\ C_6H_5{\cdot}CH(OH){\cdot}C(OH)(C_6H_5){\cdot}NH_2 = NH_3 + C_6H_5{\cdot}CH(OH){\cdot}CO{\cdot}C_6H_5.$$

That addition to the group $\cdot C(OH){:}NH$ takes place in the manner represented by the first of these equations, receives support from the observation of Busch (*Ber.*, 1904, **37**, 2691; Busch and Rinck, *Ber.*, 1905, **38**, 1761), who finds that addition of the Grignard reagent to the group $\cdot CH{:}N\cdot$ takes place in such a manner that the alkyl or aryl group attaches itself to the carbon atom and the MgX group to the nitrogen atom; the formation of α-anilinoethylbenzene, for example, from benzylideneaniline is represented by Busch as follows:



$$C_6H_5{\cdot}N{:}CH{\cdot}C_6H_5 + CH_3{\cdot}MgI = C_6H_5{\cdot}\underset{\substack{Mg\quad I}}{N}{\cdot}CH(CH_3){\cdot}C_6H_5.$$



$$C_6H_5{\cdot}\underset{\substack{Mg\quad I}}{N}{\cdot}CH(CH_3){\cdot}C_6H_5 + H_2O = C_6H_5{\cdot}NH{\cdot}CH(CH_3){\cdot}C_6H_5 + MgI(OH).$$

It is probable that mandelamide acts on the Grignard reagent in its *aci*-form as indicated in equation (1), since tautomeric compounds of the keto-enolic type are known to act on the Grignard reagent in accordance with the enolic structure. This is of little importance, however, in this case, since the same additive compound might be expected to result if mandelamide is represented by the formula $C_6H_5{\cdot}CH(OH){\cdot}CO{\cdot}NH_2$.

EXPERIMENTAL.

Action of Magnesium Phenyl Iodide on r-Mandelamide.

Methyl *r*-mandelate, prepared by the Fischer-Speier esterification method, boiled at 135—136°/13 mm., whereas Acree (*Ber*, 1904, **37**, 2767) gives the boiling point as 144°/20 mm.

r-Mandelamide is described by Zinin (*Zeitsch. Chem.*, 1868, 710) and by Beyer (*J. pr. Chem.*, 1885, [ii], **31**, 385) as melting at 132°. By the action of fuming hydrochloric acid, however, on mandelonitrile, Tiemann and Friedländer (*Ber.*, 1881, **14**, 1967) obtained a product melting at 190°, which they supposed to be the amide. The latter melting point is also ascribed by Biedermann (*Ber.*, 1891, **24**, 4083) to the amide obtained by heating for six hours under pressure at 100° with an excess of ammonia the crude product resulting from the action of an excess of acetic anhydride on mandelic acid. Michael and Jeanprêtre (*Ber.*, 1892, **25**, 1678) repeated Tiemann and Friedländer's experiments and showed that, in addition to the compound melting at 194°, the amide melting at 132° is also produced. A similar result was arrived at by Pulvermacher (*Ber.*, 1892, **25**, 2212), who found only traces of the amide melting at 132° in the action in question; when he repeated Biedermann's work, he obtained a product melting at 132° and not at 190°.

r-Mandelamide is easily prepared by the following method. A solution of methyl *r*-mandelate (48 grams) in ethyl alcohol (80 c.c.) is saturated with dry ammonia, first at the ordinary temperature and finally at the temperature of a freezing mixture of ice and salt. After three days, the crystals, which separate as lustrous leaflets, are drained off, powdered, and washed with ether. The yield is 35 grams. *r*-Mandelamide (m. p. 133—134°) is sparingly soluble in ether, and may be crystallised without much loss from benzene, from which it separates in lustrous leaflets.

r-Mandelamide (5 grams, 1 mol.) was gradually added, within an interval of twenty minutes, in quantities of about a gram each time to the Grignard reagent, prepared from 4·7 grams of magnesium (6 mols.), 40 grams of iodobenzene (6 mols.), and 75 c.c. of ether. If the action is formulated according to the scheme of Béis, the magnesium phenyl iodide was present in this case in twice the calculated amount. The addition of each portion of the amide caused a hissing noise, and the ether boiled gently, but the action was never allowed to become violent. After the reaction had subsided, the mixture was gently boiled for about eight hours, ice and dilute sulphuric acid added, and then benzene in sufficient amount to dissolve the solid product present. The ether-benzene layer was separated, the ether and benzene evaporated, and then steam passed through the residual reddish-brown oil in order to remove iodobenzene and diphenyl. The contents of the distilling flask were allowed to cool, and the semi-solid oil crystallised from methyl alcohol, when a yellow solid (1·3 grams) separated. This melted at 130—132°, and was found to consist of nearly pure benzoin. After several crystallisations from methyl alcohol, colourless needles, melting at 132·5—133·5°, were obtained.* The benzoin, obtained in this manner, gave the following result on analysis:

0·2559 gave 0·7434 CO_2 and 0·1321 H_2O. C = 79·2; H = 5·8.

$C_{14}H_{12}O_2$ requires C = 79·2; H = 5·7 per cent.

---

* The data quoted in the literature respecting the melting point of benzoin are discordant. We found that a specimen of Kahlbaum's benzoin melted at 132·5—133° after six crystallisations from methyl alcohol.

Its ethyl-alcoholic solution reduced Fehling's solution slowly in the cold and rapidly when warmed. The compound was still further characterised by conversion into benzil by means of nitric acid in the usual manner. The resulting benzil melted at 94·5—95·5° and was analysed:

0·1601 gave 0·4697 CO_2 and 0·0693 H_2O. C = 80·0; H = 4·8.
$C_{14}H_{10}O_2$ requires C = 80·0; H = 4·8 per cent.

In the hope of obtaining a better yield of benzoin, numerous experiments were also made with magnesium phenyl bromide in place of the iodide. The experimental conditions were varied in each case, but the yield of benzoin was generally much the same as that quoted in the preceding experiment. Although it was noted that *r*-mandelamide is sparingly soluble in ether, and tends to become coated with a solid when it is added to the Grignard reagent, the small yield of benzoin is not due to this cause. The yield was much the same when the Grignard reagent (4 mols.) was gradually siphoned into a warm ethereal suspension of the amide (10 grams, 1 mol.) within an interval of thirty minutes; in this case, a white product separated, which became grey when the mixture was boiled. After decomposition in the usual manner by ice and mineral acid, the product obtained from the ethereal solution was found to contain, in addition to benzoin and diphenyl, unchanged amide, since ammonia was evolved when it was heated with aqueous sodium hydroxide. In this and in other cases the reaction appears to be incomplete.

Action of Magnesium Phenyl Bromide on l-*Mandelamide. Preparation of* l-*Benzoin.*

Methyl *l*-mandelate, prepared from *l*-mandelic acid, methyl alcohol, and sulphuric acid according to the Fischer-Speier method, boiled at 135°/12 mm. and melted at 54—55°, whereas Walden (*Zeitsch. physikal. Chem.*, 1895, **17**, 703) gives 160°/32 mm. and 55° respectively. The yield is generally about 80 per cent. of the theoretical.

The following method for the preparation of *l*-mandelamide gave the best results. A current of dry ammonia is passed within an interval of one and a quarter hours into a solution of methyl *l*-mandelate (23 grams) in ethyl alcohol (30 c.c.), first at the ordinary temperature and subsequently at the temperature of a freezing mixture of ice and salt. After three days, the crystals, which separate either as leaflets or large, hexagonal, glassy prisms, are drained off, triturated with ether, and again filtered. The yield is 11 grams. A few additional grams may be obtained from the mother liquors.

l-Mandelamide, $C_6H_5{\cdot}CH(OH){\cdot}CO{\cdot}NH_2$, separates in lustrous leaflets from benzene, in which it is sparingly soluble at the ordinary temperature. Its melting point, 122°—122·5°, agrees with that given by Walden (*loc. cit.*):

0·1360 gave 0·3181 CO_2 and 0·0736 H_2O. C = 63·8; H = 6·1.
$C_8H_9O_2N$ requires C = 63·5; H = 6·0 per cent.

The rotation of successive crops from benzene solution was determined in acetone solution, this solvent having previously been selected by Walden.

$l = 2$, $c = 1·676$, $a_D^{13·8} - 2·43°$, $[a]_D^{13·8} - 72·5°$.
$l = 4$, $c = 1·6416$, $a_D^{14·4} - 4·8°$, $[a]_D^{14·4} - 73·1°$.
$l = 4$, $c = 0·6112$, $a_D^{12} - 1·77°$, $[a]_D^{12} - 72·4°$.

These values are somewhat higher than those quoted by Walden, who gives $[a]_D - 66·7°$ for $c = 1·5$ (temperature not stated).

l-Mandelamide (8 grams, 1 mol.) was gradually added in small portions within an interval of thirty minutes to the Grignard reagent, prepared from 7·5 grams of magnesium (6 mols.), 50 grams of bromobenzene (6 mols.), and 150 c.c. of ether. The mixture was then boiled for eight hours. After the addition of ice and dilute sulphuric acid, sufficient ether was added to dissolve the small amount of solid remaining in suspension after the decomposition of the magnesium additive compound. The ethereal layer was separated, the ether expelled, and steam passed through the residue for some time. From the red, semi-solid mass remaining in the distilling flask, 1·3 grams of pink crystals were obtained after crystallisation from methyl alcohol and decolorisation by animal charcoal. After recrystallisation from methyl alcohol, almost colourless needles were obtained.

l-*Benzoin*, $C_6H_5·CH(OH)·CO·C_6H_5$, melts at 131—132·5°. It is readily soluble in cold acetone or in hot methyl or ethyl alcohol, and moderately so in cold methyl or ethyl alcohol:

0·1123 gave 0·3264 CO_2 and 0·0599 H_2O. C = 79·3; H = 6·0.
$C_{14}H_{12}O_2$ requires 79·2; H = 5·7 per cent.

Its ethyl-alcoholic solution reduces Fehling's solution slowly in the cold, and rapidly when heated.

For the determination of its specific rotation in acetone solution, a specimen was dried over sulphuric acid until constant in weight:

$l = 4$, $c = 0·9232$, $a_D^{10·5} - 4·38°$, $[a]_D^{10·5} - 118·6°$.

After recrystallisation of this product from methyl alcohol, the value for the specific rotation of the recrystallised crop in acetone solution agreed with the preceding value within the limit of experimental error:

$l = 4$, $c = 1·2508$, $a_D^{12} - 5·88°$, $[a]_D^{12} - 117·5°$.

l-Benzoin (1·5 grams) was heated for about two hours with an excess of concentrated nitric acid. The mixture was poured into cold water, when the yellow oil readily solidified. After recrystallisation from ethyl alcohol, yellow needles (0·9 gram) separated, which were identified as benzil by their melting point, 93·5—94·5°, and by analysis:

0·1074 gave 0·3140 CO_2 and 0·0467 H_2O. C = 79·7; H = 4·9.

$C_{14}H_{10}O_2$ requires C = 80·0; H = 4·8 per cent.

Its solution in acetone was optically inactive.

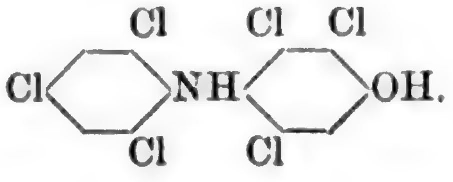
The work is being extended more particularly for the preparation of other optically active keto-alcohols.

BIRKBECK COLLEGE,
LONDON, E.C.

XXX.—*The Bromination of* p-*Hydroxydiphenylamine.*

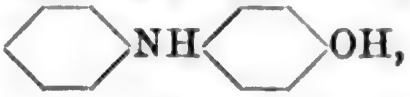
By ALICE EMILY SMITH and KENNEDY JOSEPH PREVITÉ ORTON.

IN his detailed account of *p*-hydroxydiphenylamine, Calm (*Ber.*, 1883, **16**, 2787; *ibid.*, 1884, **17**, 2431) makes no mention of any attempts to prepare chloro- or bromo-derivatives. The only halogen derivatives which have been described up to the present were obtained by us indirectly from *s*-trichloro- and *s*-tribromo-1-nitroaminobenzene, $C_6H_2Cl_3{\cdot}NH{\cdot}NO_2$ and $C_6H_2Br_3{\cdot}NH{\cdot}NO_2$ (Trans., 1905, **87**, 389; *ibid.*, 1907, **91**, 146). A hexachlorohydroxydiphenylamine, *s*-trichlorophenyltrichloro-*p*-hydroxyphenylamine, $C_6H_2Cl_3{\cdot}NH{\cdot}C_6HCl_3{\cdot}OH$, a hexabromo-derivative, *s*-tribromophenyltribromo-*p*-hydroxyphenylamine, and a pentabromo-derivative, *s*-tribromophenyldibromo-*p*-hydroxyphenylamine, $C_6H_2Br_3{\cdot}NH{\cdot}C_6H_2Br_2{\cdot}OH$, were prepared, and their constitutions partly determined by cleavage of the oxidation products, the quinoneanils, for example, $C_6H_2Cl_3{\cdot}N{:}C_6HCl_3{:}O$, into aniline and quinone. The orientation of the halogen in the phenolic nucleus remained, however, uncertain, although a suggestion, based on a hypothesis as to the method of production from the nitroamines, was put forward, namely, that in the hexahalogen compounds the three halogen atoms occupied the positions 2, 3, and 6 with respect to the imino-group. Hexachlorohydroxydiphenylamine would then have the formula:



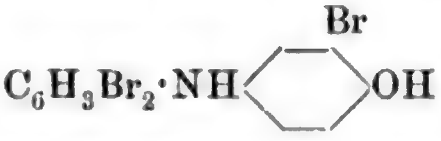
As the absence of any record in the literature indicated, the bromination of *p*-hydroxydiphenylamine has proved no easy matter. This substance is very liable to oxidation by the bromine to quinoneanil (phenyliminoquinone), $C_6H_5\cdot N\colon C_6H_4\colon O$, which is not directly brominated. Partly on this account, it is exceedingly difficult to avoid the formation of a mixture of bromo-derivatives, separation of which either proved impracticable, or only possible with great loss of material.

In one particular, the preparation of the bromo-derivatives was simplified, in that isomerides do not seem to be formed under any circumstances. Notwithstanding the presence of the two benzene nuclei,

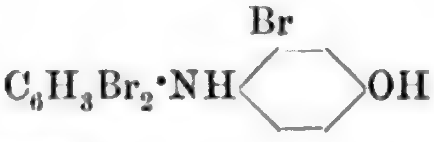


and the two directing groups, the imino-group, which may influence the bromination in both nuclei, and the hydroxyl group, which will determine the position of the bromine in the phenolic nucleus, the introduction of bromine appears to follow a single invariable course. Thus, for example, in the preparation of the tribromo-derivative from *p*-hydroxydiphenylamine, it would seem highly probable that a mixture of two or three tribromo-compounds would be produced. Such was not found to be the case; there was no indication of the presence of even traces of a second compound. Similarly, in the preparation of the tetrabromo- from the tribromo-derivative, the formation of two isomerides at least would be anticipated, whereas only a single substance resulted.

All our attempts to prepare a monobromo- and a dibromo-derivative have so far failed. Variation in solvent or the use of bromine vapour all lead to a tribromohydroxydiphenylamine, two-thirds of the hydroxydiphenylamine remaining unchanged. This tribromo-derivative has two bromine atoms in the phenyl nucleus, occupying the 2:4-positions with respect to the imino-group, and one bromine atom in the phenyl nucleus, but there is no means of ascertaining which of the two possible formulæ:

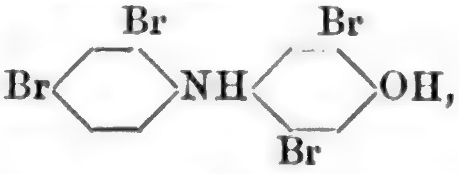


and



represents the orientation in this nucleus.

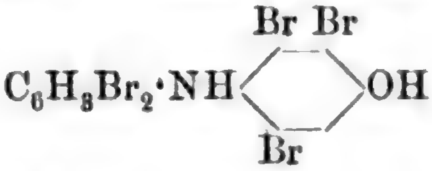
Bromination of the tribromo-derivative yields a single tetrabromohydroxydiphenylamine of the constitution:



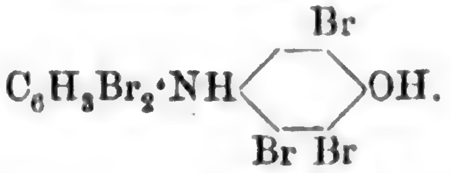
the fourth bromine atom entering the phenolic nucleus.

lles

The fifth bromine atom also enters the phenolic nucleus, but it is impossible to decide at present which of the two different positions is taken up. The compound must be represented by either

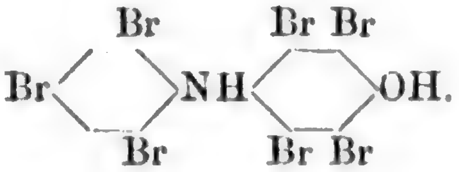


or



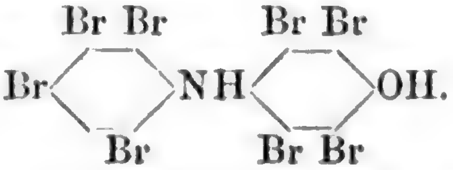
Either of these compounds would be isomeric with the pentabromohydroxydiphenylamine obtained from *s*-tribromonitroaminobenzene (*loc. cit.*), since the latter had three bromine atoms in the phenyl nucleus.

All attempts to convert the pentabromo- into a hexabromo-derivative failed. Either bromination did not occur, or a heptabromo-derivative was formed. If the two entering bromine atoms take up positions in accordance with the "ortho-para" rule, only one heptabromo-derivative is possible, namely, that possessing the constitution represented by



Cleavage of the corresponding quinoneanil showed that such was the fact.

Large excess of bromine in the absence of solvent, finally produces the octabromo-derivative,



Each bromohydroxydiphenylamine can be quantitatively oxidised to a quinoneanil (phenyliminoquinone), from which it is as easily regenerated on reduction. The colour of the quinoneanils becomes more intense as the proportion of bromine increases, the unsubstituted being scarlet and the hepta- and octabromo-derivatives so dark a purple or magenta as to appear black. The quinoneanils are hydrolysed by sulphuric acid to aniline and quinone, thus:

$$C_6H_3Br_2{\cdot}N{:}C_6HBr_3{:}O + H_2O = C_6H_3Br_2{\cdot}NH_2 + O{:}C_6HBr_3{:}O,$$

a reaction which gives a simple means of determining the position and generally the orientation of the bromine atoms.

EXPERIMENTAL.

p-*Hydroxydiphenylamine.*—The hydroxydiphenylamine was prepared d purified by Calm's method (*loc. cit.*), namely, condensation of iline with quinol in the presence of calcium chloride at a high temperature. In addition to the dibenzoyl derivative described by him, we have prepared a monobenzoyl derivative,

$$C_6H_5{\cdot}NH{\cdot}C_6H_4{\cdot}O{\cdot}CO{\cdot}C_6H_5,$$

which is alone formed when the benzoylation is carried out in pyridine.

Twenty-five c.c. of benzoyl chloride are added to a solution of 3 grams of the material in 12 c.c. of pyridine, the mixture being kept for twenty-four hours. The solid, which is obtained on dilution with dilute sulphuric acid, is collected and washed with water and aqueous sodium carbonate, and recrystallised first from alcohol and then from petroleum (b. p. 120°). It crystallises in yellowish-white, lustrous plates, melting at 114—115°. Since it is insoluble in aqueous or alcoholic sodium hydroxide, the benzoyl group has replaced the hydrogen of the hydroxyl group:

0·2501 gave 9·8 c.c. of moist nitrogen at 9·4° and 773 mm. N = 4·79.

$C_{19}H_{15}O_2N$ requires N = 4·84 per cent.

An attempt to prepare a monoacetyl derivative was unsuccessful, Calm's diacetyl derivative being the sole product.

Tribromohydroxydiphenylamine. 2 : 4-*Dibromophenylbromo*-4-*hydroxyphenylamine*, $C_6H_3Br_2{\cdot}NH{\cdot}C_6H_3Br{\cdot}OH$.

The bromination of *p*-hydroxydiphenylamine is carried out in glacial acetic acid solution in the presence of sodium acetate. After some experience, good yields of pure material can be obtained, but success depends greatly on the rate of addition of the bromine and the temperature. Unless the latter is kept low and the addition of the bromine made slowly and with efficient stirring, considerable quantities of more highly brominated compounds are formed.

7·4 Grams of the diphenylamine and 9·6 grams of anhydrous sodium acetate are dissolved in 200 c.c. of glacial acetic acid. To this mixture a solution of 19·2 grams of bromine in 100 c.c. of glacial acetic acid is slowly added, the mixture being both cooled and stirred during the operation. As the bromine is added, the originally colourless liquid becomes of a deep olive-green.

It is very important that both the materials and the solvent should be as nearly as possible anhydrous. In the presence of even small quantities of water, the bromine acts as an oxidising agent, converting the hydroxydiphenylamine into a quinoneanil (see introduction).

Before isolating the tribromo-derivative from the acetic acid, it is advisable to reduce any quinoneanil which may have been formed by warming with a small quantity of zinc dust. The colourless filtrate is then mixed with 80 c.c. of water, whereupon tribromohydroxydiphenylamine (11·6 grams) crystallises out in white needles which are approximately pure. Addition of a further 80 c.c. of water to the warm filtrate causes the separation of a smaller quantity (2·4 grams) of a somewhat less pure material.

The material thus isolated contains a small quantity of a tetrabromohydroxydiphenylamine. The two compounds can, however, be separated by dissolving the mixture in petroleum (b. p. 120°), in which the tribromo-derivative is very sparingly soluble, whilst the tetrabromo-derivative dissolves readily. The former crystallises in long, colourless needles, melting at 153°, and is readily soluble in alcohol, acetic acid, benzene, or acetone, but somewhat less so in chloroform, from which solvent it can be recrystallised. It dissolves in aqueous sodium hydroxide. With hydrochloric acid in anhydrous solvents, it does not give a precipitate of the hydrochloride as does the unsubstituted hydroxydiphenylamine, but the solution in sulphuric acid has the characteristic green coloration of solutions of the salts; on adding water, the hydroxydiphenylamine is precipitated unchanged:

0·1635 gave 0·2170 AgBr. Br = 56·49.

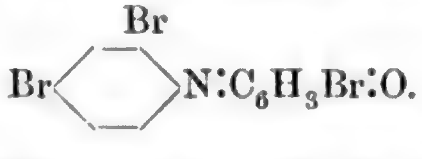
$C_{12}H_8ONBr_3$ requires Br = 56·85 per cent.

Tribromobenzoxydiphenylamine, $C_6H_3Br_2\cdot NH\cdot C_6H_3Br\cdot O\cdot CO\cdot C_6H_5$, was prepared by means of benzoyl chloride and pyridine. One gram of the hydroxydiphenylamine was dissolved in 5 c.c. of pyridine and treated with 0·5 c.c. of benzoyl chloride. The mixture was kept for three days, when crystalline aggregates had separated. After removal of pyridine by treatment with dilute sulphuric acid, the crystals were collected and washed with aqueous sodium carbonate. The compound, which is soluble in all the usual organic solvents, was finally purified by recrystallisation from petroleum (b. p. 120°), separating in white, prismatic crystals, melting at 147°:

0·1514 gave 0·1633 AgBr. Br = 45·9.

$C_{19}H_{12}O_2NBr_3$ requires Br = 45·6 per cent.

Tribromoquinoneanil. 2 : 4-*Dibromophenyliminobromoquinone*,



The tribromohydroxydiphenylamine can be oxidised in benzene solution by mercuric oxide, or in acetic acid solution by nitrous acid or chromic acid, to the corresponding quinoneanil. The conversion is preferably carried out by the reagent last mentioned.

One gram of the hydroxydiphenylamine, dissolved in 50 c.c. glacial acetic acid, is added to a solution of 0·24 gram of chromium trioxide (50 per cent. excess) in 50 c.c. acetic acid. The reaction is very rapid. Sixty c.c. of water are then gradually added, whereupon a separation of bright crimson crystals takes place. The material, which is readily soluble in the usual organic solvents, is recrystallised from petroleum (b. p. 90°). It separates in aggregates of long, red needles, which melt at 112°:

0·1895 gave 0·2555 AgBr. Br = 57·37.
0·2990 „ 9·0 c.c. of moist nitrogen at 16·1° and 752·4 mm. N = 3·47.
$C_{12}H_6ONBr_3$ requires Br = 57·24; N = 3·34 per cent.*

The quinoneanil can be very readily converted into the hydroxydiphenylamine in acetone solution by zinc dust and acetic acid.

In the oxidation of the hydroxydiphenylamine, the use of insufficient oxidising agent is followed by the formation of a deep purple, crystalline solid, melting at 142°. It is less soluble than the quinoneanil, into which it is converted by further treatment with the oxidising agent. Moreover, on reducing this substance in acetone solution with zinc dust and acetic acid, the original hydroxydiphenylamine is formed. This compound is probably a complex condensation product of molecular proportions of quinoneanil and hydroxydiphenylamine analogous to the quinhydrones.

Constitution of the Tribromoquinoneanil.—Quinoneanils are readily hydrolysed by sulphuric acid, which may be when necessary diluted with acetic acid. Generally, the aniline and quinone thus formed can be isolated with ease, but in this case considerable difficulty was experienced. A solution of 0·5 gram of the quinoneanil in 25 c.c. of acetic acid was mixed with 18 grams of sulphuric acid dissolved in 10 c.c. of acetic acid. On warming the deep red liquid for a few minutes, the colour changed to a pale brown. Very little solid separated on addition of water, and it could not be recognised as monobromoquinone. The mother liquor was made alkaline by means of sodium hydroxide, and then distilled in a current of steam. The colourless, crystalline material which distilled melted at 79·5°, and a mixture with 2 : 4-dibromoaniline, which has the same melting point, melted at 79—80°. The substance was heated with acetic anhydride, and yielded a derivative which melted at 143° and did not lower the melting point of 2 : 4-dibromoacetanilide.

*Attempts to Prepare Mono- and Di-bromo-*p-*hydroxydiphenylamine.*—A number of attempts were made to prepare monobromohydroxydiphenylamine, using molecular proportions of bromine and *p*-hydroxydiphenylamine in acetic acid or chloroform, the bromine being cautiously and gradually added to the solution of the diphenylamine. With both solvents, a green solution was obtained. The acetic acid solution was treated with a little zinc dust in order to reduce quinoneanil, and then precipitated with sodium acetate solution, the object of the latter being to decompose any soluble hydrobromide. The solid which separated was of very indefinite melting point, but on recrystallisation from dilute alcohol gave crystals of the tribromo-derivative. No other material besides unchanged *p*-hydroxydiphenylamine could be discovered in the mother liquors. Evaporation of the solvent from the chloroform solutions left a green, oily hydrobromide, which on treatment with aqueous sodium hydrogen carbonate yielded a solid. Crystallisation from petroleum did not bring about any separation of this solid, but crystallisation from dilute acetic acid led immediately to the isolation of the tribromo-*p*-hydroxydiphenylamine.

---

* We are indebted to Mr. Emrys Morgan for the analyses of this substance.

After these failures, an attempt was made to brominate the hydroxydiphenylamine in the solid state with the vapour of bromine. The substance in a finely-powdered condition was spread out on a clock glass and treated with the vapour of one molecular proportion of bromine. The latter had entirely disappeared in three days, the substance becoming green in colour. The green solid was treated with sodium carbonate, and then extracted with petroleum (b. p. 85—105°). The melting point, originally low and indefinite, gradually rose, and, after recrystallisation of the material of the highest melting point from dilute acetic acid, tribromohydroxydiphenylamine was isolated. From the first petroleum mother liquors, the unsubstituted hydroxydiphenylamine was obtained in a pure state.

Treatment of *p*-hydroxydiphenylamine in acid solution with alkaline sodium hypobromite, prepared from one molecular proportion of bromine, leads mainly to oxidation and cleavage; quinone can be isolated in quantity.

Tetrabromohydroxydiphenylamine. 2 : 4-*Dibromophenyl*-2′ : 5′-*dibromo*-4′-*hydroxyphenylamine*, $C_6H_3Br_2\cdot NH\cdot C_6H_2Br_2\cdot OH$.

The tetrabromohydroxydiphenylamine was in the first instance isolated from the petroleum mother liquors obtained in the purification of the tribromohydroxydiphenylamine. Although the proportion of the tetrabromo-derivative is very small, the great difference in the solubility of the two substances in this solvent permits of a sharp separation. The residue left on evaporating the petroleum mother liquor was dissolved in glacial acetic acid, to which when cold a few drops of water were added, whereupon colourless needles separated. After repetition of this procedure the melting point was constant at 144°:

0·1929 gave 0·2896 AgBr. Br = 63·87.

$C_{12}H_7ONBr_4$ requires Br = 63·85 per cent.

A number of attempts were made to prepare the tetrabromohydroxydiphenylamine; on the one hand, by brominating the tribromo-derivative in acetic acid solution either with or without sodium acetate, and, on the other, by direct bromination of the *p*-hydroxydiphenylamine, but in no case was more than a very small amount of the substance isolated. The tribromo-derivative was mainly oxidised to quinoneanil, and the *p*-hydroxydiphenylamine was converted into the tribromo-derivative and then oxidised.

On attempting the bromination in chloroform, however, better results were obtained. The *p*-hydroxydiphenylamine, when small quantities are used, yields an impure specimen of the tetrabromo-derivative, but, if the bromination is attempted on a large scale, a complex mixture of bromo-derivatives results.

The tetrabromohydroxydiphenylamine, however, can be readily prepared from the tribromo-derivative in chloroform solution.

Preparation of Tetrabromohydroxydiphenylamine.—To a suspension of 5 grams of the tribromohydroxydiphenylamine in 100 c.c. of chloroform one molecular proportion (2·01 grams) of bromine is gradually added whilst the mixture is boiled. Hydrogen bromide is slowly evolved, and the whole solid finally dissolves. The solvent is then evaporated, and the residue is crystallised by dissolving in glacial acetic acid and then adding a trace of water.

Tetrabromohydroxydiphenylamine crystallises in aggregates of white needles, melting at 143—144°. It is far more readily soluble in chloroform or petroleum than the tribromo-derivative, but is not so readily soluble in acetic acid containing a small quantity of water.

Tetrabromobenzoxydiphenylamine,

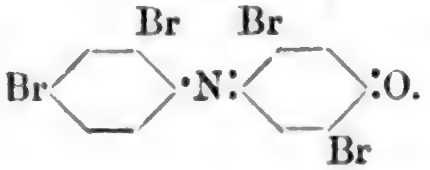
$$C_6H_3Br_2\cdot NH\cdot C_6H_2Br_2\cdot O\cdot CO\cdot C_6H_5.$$

—The benzoylation was readily carried out in pyridine solution, when the benzoyl derivative separated almost immediately on adding the benzoyl chloride. The benzoyl derivative is best purified by recrystallisation from petroleum (b. p. 120°), from which it separates in snow-white aggregates of needles, melting at 178°. It is insoluble in sodium hydroxide, and sparingly soluble in the ordinary organic solvents:

0·1477 gave 0·1827 AgBr. Br = 52·64.

$C_{19}H_{11}O_2NBr_4$ requires Br = 52·87 per cent.

Tetrabromoquinoneanil. 2:4-*Dibromophenylimino*-2′:5′-*dibromoquinone*,



The tetrabromohydroxydiphenylamine was oxidised in glacial acetic acid solution with considerable excess of chromium trioxide at the ordinary temperature. On adding water, branching, twig-like groups of needles separated, melting at 159°. Subsequent recrystallisation did not change the melting point. This compound is very soluble in chloroform or benzene; it is moderately soluble in cold acetic acid, and very sparingly so in cold alcohol or petroleum. These properties permit of its being readily recrystallised either from petroleum or alcohol. It forms dark red needles with a bronzy lustre:

0·1875 gave 0·2816 AgBr. Br = 63·91.

$C_{12}H_5ONBr_4$ requires Br = 64·11 per cent.

Hydrolysis of the Quinoneanil.—One gram of the tetrabromoquinoneanil was dissolved in 25 c.c. of concentrated sulphuric acid, forming a deep crimson solution. On adding rapidly 20 c.c. of water, the mixture being allowed to become heated, the red colour was replaced by a pale yellow colour. Five c.c. more water were now added, whereupon a yellow solid separated. This precipitate was collected and recrystallised from alcohol. It formed yellow, iridescent plates, melting at 186·5°, the melting point of 2 : 5-dibromoquinone. Analysis showed it to be this compound:

0·1602 gave 0·2261 AgBr. Br = 60·1.

$C_6H_2O_2Br_2$ requires Br = 60·13 per cent.

The sulphuric acid mother liquor, from which the quinone was separated, was distilled in a current of steam, when a solid, crystallising in white needles, passed over. Its melting point and the melting point of the acetanilide, obtained from it by treatment with acetic anhydride, showed it to be 2 : 4-dibromoaniline.

Pentabromohydroxydiphenylamine. 2 : 4-*Dibromophenyltribromo*-4′-*hydroxyphenylamine*, $C_6H_3Br_2{\cdot}NH{\cdot}C_6HBr_3{\cdot}OH$.

Indications of the existence of pentabromohydroxydiphenylamine were obtained in an attempt to prepare the tetrabromo-derivative directly from hydroxydiphenylamine dissolved in chloroform, the calculated quantity of bromine being used; but recrystallisation of the product from chloroform or acetic acid failed to free the pentabromo-derivative from a more highly-brominated material. The pentabromo-derivative was subsequently prepared by treatment of the tetrabromohydroxydiphenylamine in chloroform solution with one molecular proportion of bromine. Both boiling the mixture and heating under pressure at 100° failed to make the bromination anything but a very slow process. Moreover, the product of the reaction was not the pure pentabromo-derivative, and the latter could only be isolated, and then with considerable loss, by repeated recrystallisation from chloroform. It was found, however, that the yield was greatly improved when the chloroform solution was exposed to sunlight. The following procedure gave a satisfactory result. One gram of the tetrabromo-derivative was dissolved in 60 c.c. of chloroform, and one molecular proportion of bromine (0·3 gram) added. The mixture, which was contained in a stoppered bottle, was then exposed to sunlight until the colour of the bromine had disappeared, a few hours to several days being necessary for this change, according to the intensity of the light. During the reaction, colourless needles gradually separated. They were collected and washed with chloroform, and when dried weighed 0·75 gram. They melted at 206—207°, and, after recrystallisation from chloroform or acetic acid, at 207—208°. Analysis showed that these crystals were the pentabromo-derivative:

0·1684 gave 0·2719 AgBr. Br = 68·71.

$C_{12}H_6ONBr_5$ requires Br = 68·94 per cent.

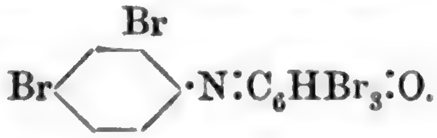
With the exception of acetone, this compound is but sparingly soluble in the usual organic solvents, and can be readily crystallised from chloroform or acetic acid.

Pentabromobenzoxydiphenylamine, $C_6H_3Br_2 \cdot NH \cdot C_6HBr_3 \cdot O \cdot CO \cdot C_6H_5$—The benzoylation is carried out by treatment with benzoyl chloride in pyridine solution, and the benzoxy-derivative isolated by treatment with dilute sulphuric acid. Purification is effected by recrystallisation from petroleum (b. p. 120°), from which solvent it separates in small needles, melting at 176°. This compound is sparingly soluble in all the usual solvents:

0·1260 gave 0·1714 AgBr. Br = 57·89.

$C_{19}H_{10}O_2NBr_5$ requires Br = 58·46 per cent.

Pentabromoquinoneanil. 2:4-Dibromophenyliminotribromoquinone,



Owing to the insolubility of the pentabromohydroxydiphenylamine in acetic acid, 100 c.c. of acetic acid at 30° are required to dissolve 0·5 gram. This solution was added to some excess of chromium trioxide in 25 c.c. of the same solvent, when oxidation took place rapidly. Separation of the quinoneanil was brought about by the addition of 50 c.c. of water. It was purified by crystallisation from petroleum (b. p. 120°), and separated in dark crimson prisms, which exhibited very marked twinning and melted at 157°. It is readily soluble in chloroform, benzene, or acetone, and sparingly so in alcohol or petroleum:

0·1855 gave 0·3002 AgBr. Br = 68·87.

$C_{12}H_4ONBr_5$ requires Br = 69·18 per cent.

Hydrolysis of Pentabromoquinoneanil.—The hydrolysis was carried out in the manner described above, tribromoquinone separating directly from the diluted solution of the quinoneanil in sulphuric acid. On recrystallising the quinone from alcohol, it was obtained in characteristic golden plates, melting at 147°, and not lowering the melting point of a specimen prepared directly. The acid mother liquor from the quinone was rendered alkaline with sodium hydroxide, and distilled in a current of steam. 2 : 4-Dibromoaniline passed over, and was recognised in the usual manner.

Heptabromohydroxydiphenylamine. s-*Tribromophenyl*-2′ : 3′ : 5′ : 6′-*tetrabromo*-4′-*hydroxyphenylamine*, $C_6H_2Br_3 \cdot NH \cdot C_6Br_4 \cdot OH$.

Numerous attempts to brominate the pentabromo-derivative by treatment in chloroform or acetic acid solution, either at a high temperature under pressure or by exposure to sunlight, led to no result. On heating the pentabromo-derivative in the absence of a solvent with one molecular proportion of bromine in a sealed tube at 100°, bromination took place slowly. Examination of the product showed, however, that the hexabromo-derivative is not formed, but that half of the pentabromo-derivative was converted into heptabromohydroxydiphenylamine. In subsequent experiments, when two molecular proportions of bromine were used, the yield of heptabromohydroxydiphenylamine was quantitative. The heptabromo-compound could also be prepared directly from the unsubstituted *p*-hydroxydiphenylamine. For this purpose, 2 grams of the hydroxydiphenylamine were placed in a stoppered bottle and moistened with 3 c.c. of chloroform, and the calculated quantity (seven molecular proportions) of bromine introduced. The bottle was kept in a warm place, the evolution of hydrogen bromide being at first very rapid; but later it was necessary, in order to complete the bromination, to heat the bottle on the water-bath. All the solvent was evaporated, and the solid residue dissolved in boiling acetic acid. On cooling, the heptabromo-derivative separated in an almost pure state. The yield was small, but this procedure is, however, to be preferred to the bromination of the pentabromo-compound.

The substance can be recrystallised from acetic acid, from which solvent it separates in characteristic, lustrous, transparent rhombs, a feature which distinguishes this compound from all the other bromohydroxydiphenylamines herein described. It melts at 173°, and is more soluble in the usual solvents than the pentabromo-derivative, being particularly soluble in chloroform, benzene, or acetone, and less so in acetic acid, alcohol, or petroleum:

0·107 gave 0·1893 AgBr. Br = 75·29.
0·1578 ,, 0·2808 AgBr. Br = 75·73.

0·1479 gave 0·2632 AgBr. Br = 75·73.

$C_{12}H_4ONBr_7$ requires Br = 75·86 per cent.

The first of the analyses was that of a specimen prepared from the pentabromo-derivative, whereas the two latter were of specimens prepared directly from *p*-hydroxydiphenylamine.

Heptabromobenzoxydiphenylamine, $C_6H_2Br_3\cdot NH\cdot C_6Br_4\cdot O\cdot CO\cdot C_6H_5$.—This compound was prepared in the usual manner from the heptabromo-derivative. It can be recrystallised from alcohol or acetic acid, and forms characteristic, transparent rhombs, melting at 206°. Its crystalline habit is in marked contrast to that of the other benzoyl derivatives. It is very sparingly soluble in all the usual organic solvents with the exception of chloroform :

0·1101 gave 0·1715 AgBr. Br = 66·29.

$C_{19}H_8O_2NBr_7$ requires Br = 66·49 per cent.

Heptabromoquinoneanil. s-*Tribromophenyliminotetrabromoquinone*, $C_6H_2Br_3\cdot N{:}C_6Br_4{:}O$.

This quinoneanil was prepared by adding a warm solution of 0·5 gram of heptabromohydroxydiphenylamine in 50 c.c. of acetic acid to a solution of some excess of chromium trioxide in 25 c.c. of acetic acid. The liquid rapidly became deep purple, and on adding water a black, crystalline powder separated. This substance is moderately soluble in chloroform, acetone, or benzene, forming deep violet solutions, but it can be recrystallised from alcohol, in which it dissolves sparingly. It forms lustrous, crystalline spicules, which are black by reflected light, but puce-brown by transmitted light. It melts at 185° :

0·1052 gave 0·1874 AgBr. Br = 75·81.

$C_{12}H_2ONBr_7$ requires Br = 75·72 per cent.

The quinoneanil dissolves but sparingly in concentrated sulphuric acid. Cautious addition of water to the deep crimson solution results in hydrolysis, and, on cooling, bromoanil separates. It was recrystallised from benzene, and separated in the usual lustrous crystals, which were not molten at 277°, and readily sublimed.

On further addition of water to the acid mother liquor, colourless needles of *s*-tribromoaniline are deposited. After recrystallisation from alcohol, they melted at 119°, and did not lower the melting point of a specimen of *s*-tribromoaniline.

Octabromohydroxydiphenylamine. 2 : 3 : 4 : 6-*Tetrabromophenyl*-2′ : 3′ : 5′ : 6-*tetrabromo*-4′-*hydroxyphenylamine*, $C_6HBr_4\cdot NH\cdot C_6Br_4\cdot OH$.

In one of the attempts to prepare hexabromohydroxydiphenylamine, the pentabromo-derivative was dissolved in some excess of bromine, and the bromine allowed to evaporate at the ordinary temperature. A yellow, crystalline solid remained. On repeated recrystallisation from glacial acetic acid, the melting point finally rose to 222°. Analysis showed that the material was an octabromo-derivative:

0·1214 gave 0·2226 AgBr. Br = 78·03.

$C_{12}H_8ONBr_8$ requires Br = 78·32 per cent.

The octabromo-derivative crystallises in highly-refractive, lustrous prisms from acetic acid, it is moderately soluble in chloroform, benzene, or acetone, and sparingly so in alcohol or acetic acid.

Octabromoquinoneanil. 2:3:4:6-*Tetrabromophenylimino*-2′:3′:5′:6′-*tetrabromoquinone*, $C_6HBr_4\cdot N\colon C_6Br_4\colon O$.

The oxidation of the octabromohydroxydiphenylamine was carried out with chromic acid in the usual manner. The low solubility of the hydroxy-compound necessitated the use of a large quantity of solvent. As the oxidation proceeded, the solution became reddish-violet. On adding water, which caused the separation of the quinoneanil as a black, crystalline powder, the liquid became completely decolorised.

This substance is readily soluble in chloroform, sparingly so in alcohol, from which it can be recrystallised, and moderately so in acetone. It was purified by recrystallisation from alcohol, and then from slightly diluted acetone. In crystalline habit and in the colour of its solutions, it resembles the heptabromo-compound. The melting points also are nearly identical, the octabromo-derivative melting at 183°, whilst the heptabromo-compound melts at 185°:

0·0875 gave 0·162 AgBr. Br = 78·79.

$C_{12}HONBr_8$ requires Br = 78·52 per cent.

Cleavage of the quinoneanil is effected in the usual manner. The bromoanil separates directly from the acid solution, whilst the tetrabromoaniline is obtained on further dilution of the mother liquor. The melting point of the aniline was that of 2:3:4:6-tetrabromoaniline, namely, 115°.

The authors wish to take this opportunity of expressing their indebtedness to the Grants Committee of the British Association for grants which have partly defrayed the cost of this research.

UNIVERSITY COLLEGE OF NORTH WALES,
BANGOR.

XXXI.—*The Reducibility of Magnesium Oxide by Carbon.*

By ROLAND EDGAR SLADE, M.Sc.

THE investigation already described in a preliminary note (Proc., 1907, **23**, 152) has been continued and extended, and, since the results now appear to be conclusive, it is thought advisable to publish a complete account of the work.

Considerable interest attaches to the reaction between magnesia and carbon, since, of all the metallic oxides, magnesia has longest withstood attempts to effect its direct reduction. Moissan (*The Electric Furnace*, p. 224) states that "Magnesia may be fused and kept liquid in a carbon crucible without being reduced."

In some electric furnace work in which it was necessary to brasque carbon crucibles with magnesia, it was observed that the walls of the crucible were considerably corroded in those places where they had been in contact with the strongly heated magnesia. This led to the investigation of the cause of the attack.

On consideration, it became clear that any reduction products formed under these conditions might escape notice on account of the ready volatility of magnesium and the ease with which it reacts with carbon monoxide and other gases with which it would come in contact.

During the progress of this work, Lebeau has published a paper on the subject (*Compt. rend.*, 1907, **144**, 799), but he considers that the reaction only occurs between the vapours of carbon and magnesia at the high temperature of the electric arc. By the use of a more suitable form of electric furnace, in which the heating is under better control, it is easy to prove that reduction occurs at far lower temperatures.

EXPERIMENTAL.

Series I.—A small piece of magnesia placed on a carbon plate was heated for some minutes in a horizontal carbon-tube resistance furnace to a temperature above the fusing point of magnesia; the magnesia was found to have penetrated through the carbon plate.

With the object of collecting any magnesium which might be set free by this reaction, it was decided to employ molten copper in conjunction with the mixture of magnesia and carbon. The copper served as a solvent and condenser of the metal vapour, the method being similar to that employed for aluminium by Hutton and Petavel (*Phil. Trans.*, 1908, *A*, **207**, 446). Alloys containing up to 2 per cent. of magnesium were prepared in this way, but the method is not suitable

Series II.—A mixture of magnesia and carbon, the magnesia being in excess, was placed in a graphite boat in a horizontal carbon-tube resistance furnace. A rapid stream of nitrogen was passed through the tube during the heating, which was continued for twenty minutes at about 1900°. The exact temperature could not be determined, owing to the formation of an opaque film across the cool end of the tube. On examining the boat, it was found to contain unfused magnesia, quite white and free from carbon. A quantity of carbon insufficient to reduce all the magnesia having been present, all the carbon was used up, leaving an excess of magnesia in the boat. This shows that the reduction takes place below the fusion point of magnesia.

In another experiment, a mixture of carbon and magnesia was placed in a graphite boat in a furnace similar to that used in the last experiment. A rapid stream of hydrogen was passed through the furnace while the temperature was slowly raised, readings of the temperature being taken with the Wanner optical pyrometer; at about 1670°, it was noticed that the tube became filled with fumes which settled, forming a grey film; this was found to contain traces of magnesium carbide. The temperature of reduction of magnesia by carbon thus probably begins a little below 1700°.

Series III.—In these experiments, a mixture of magnesia and carbon was placed in a graphite boat, which was heated in a vacuum by the resistance which it offered to the passage of an electric current.

In order more carefully to examine the products of the reaction and to keep a close observation on the process, an electrically heated device was mounted in a glass apparatus similar to that used by Pring and Hutton in the synthesis of acetylene (Trans., 1906, **89**, 1593). A carbon rod held in graphite end-pieces, which were mounted in water-cooled brass tubes, served as the heater, the rod being grooved out into the form of a boat to support the mixture of magnesia and carbon. The apparatus was exhausted and the experiments made in a vacuum, the gas generated being pumped out and subsequently analysed.

These experiments proved most successful, the magnesia being reduced and the inner surface of the glass globe above the heated rod being coated with a bright mirror of magnesium.

In one experiment, a carbon rod 10 cm. long and 0·7 cm. in diameter was used, and the following are particulars of the experiment:

Time in minutes.	Amperes.	Volts.	Pressure in mm.	Remarks.
0	60	12·7	2·7	—
1	100	16·8	45	—
2	115	16·2	—	—
4	—	—	80	—
5	—	—	—	35 c.c. pumped out
6	—	—	—	58 ,, ,,
7	120	16·2	42	—
14	120	16·0	44	—
15	(current stopped)			
85	—	—	24	52 c.c. pumped out
90	—	—	7·5	—

The temperature was approximately 1900° as determined with the Wanner optical pyrometer. The gases pumped out were subsequently analysed.

The inside of the globe was coated with a bright silver-like mirror. This metallic-looking deposit dissolved readily with effervescence in dilute hydrochloric acid, and oxidised to a white oxide when heated in air. Further proof of the reduction of the magnesia having been effected is given by the gas analysis. The last sample of gas taken gave on analysis $CO = 57·4$, $H = 38·1$, $N = 4·4$ per cent. After allowing for the carbon monoxide produced by the reaction of the small amount of residual water, this leaves a considerable excess of carbon monoxide produced by actual reduction of the magnesia. Blank experiments in which carbon rods were similarly heated in the absence of magnesia served to confirm this conclusion.

Series IV.—A vacuum having been successfully employed in removing the carbon monoxide from the magnesium before the reverse reaction $CO + Mg = C + MgO$ was complete, other methods were attempted for removing this carbon monoxide and facilitating the condensation of the magnesium.

A mixture of magnesia and carbon was heated to about 1900° in a rapid stream of hydrogen, which then passed through a water-cooled copper tube serving as a condenser.

The apparatus used is shown in Fig. 2. It consists of a retort made up of two carbon crucibles, one inverted over the other—the two being held together by graphite supports. Into a hole in the top of this retort a carbon tube is ground, which serves as an inlet for the hydrogen. In the side near the top, an outlet hole is bored and ground to fit the water-cooled copper tube.

The retort was charged with a mixture of 40 grams of magnesia and 12 grams of carbon (petroleum coke), and then embedded in a granular carbon resistance furnace.

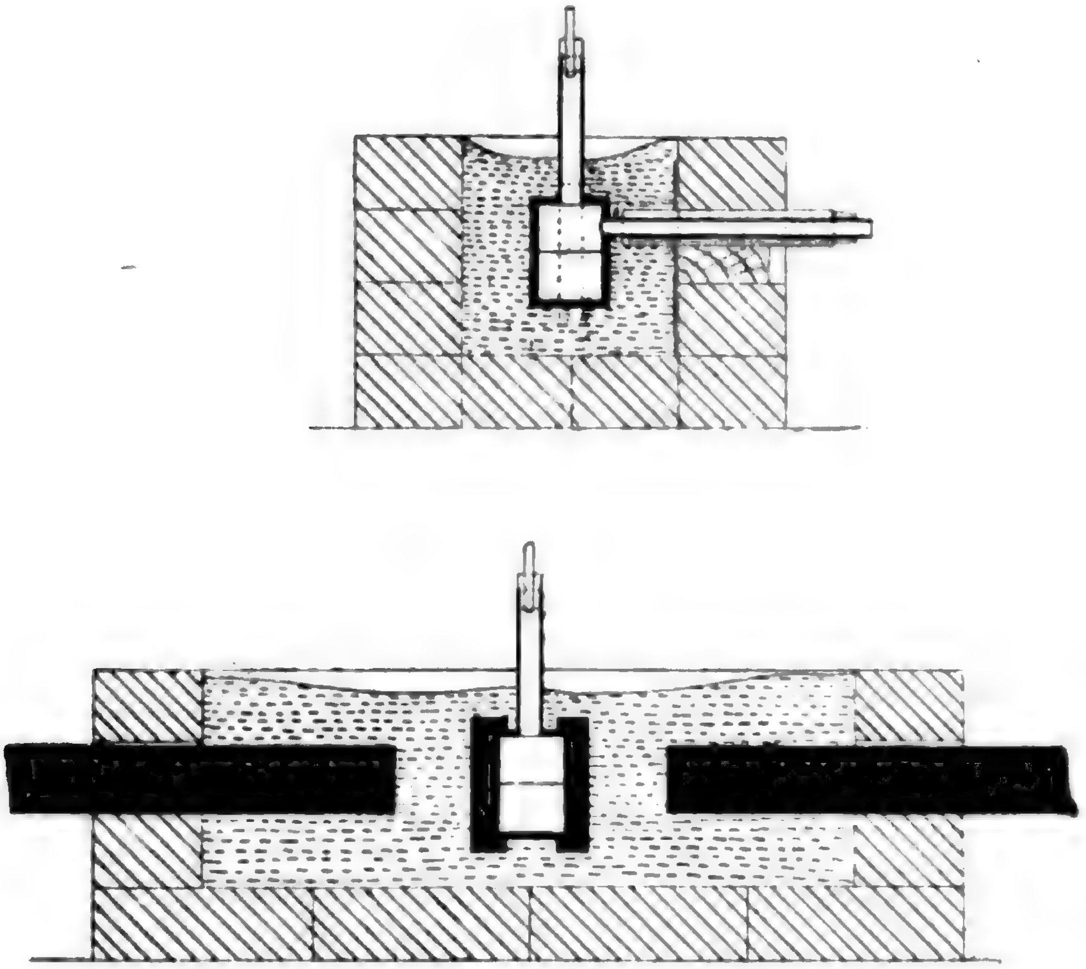
The following are particulars of the power used :

Time in minutes.	Amperes.	Volts.	Time in minutes.	Amperes.	Volts.
0	50	70	30	450	23
5	100	—	65	450	21
7	140	58	90	450	20
18	450	26			

The temperature of the retort was probably 1800° to 1900°; it was certainly below the fusion point of magnesia.*

In the condenser tube were found about 2 grams of a grey powder. This, on exposure to the atmosphere, gave off a little ammonia, which was recognised by its odour and by its action on litmus paper. The powder was treated with dilute hydrochloric acid, when 70 c.c. of gas were evolved, which, on analysis, gave $H_2S = 49{\cdot}94$, $C_2H_2 = 7{\cdot}82$, $H = 42{\cdot}13$ per cent. A residue of carbon was left undissolved, and the solution was tested and found to contain only magnesium; it was quite free from calcium. The powder must therefore have consisted of a mixture of magnesium together with its nitride, sulphide, carbide, and oxide, and some carbon.

Fig. 2.



Granular carbon resistance furnace and retort.

Scale 1/12th.

---

* About 1920°, according to H. M. Goodwin and R. D. Mailey, *Trans. Amer. Electrochem. Soc.*, 1906.

The nitride would be formed from the heated magnesium on its coming into contact with nitrogen, the sulphide from its coming into contact with hydrogen sulphide, the sulphur being derived from the carbon; it is a well-known fact that the sulphur always present in commercial carbon can be partly converted into hydrogen sulphide by heating to 2000° in a stream of hydrogen. The carbon and magnesia probably resulted from the interaction of heated magnesium and carbon monoxide.

In another experiment, a similar apparatus was used, except that in place of the water-cooled copper condensing tube a carbon tube was used, and a piece of aluminium weighing 60 grams was placed in the retort along with the charge of magnesia and carbon. A swift stream of hydrogen was passed as before. It was hoped that the aluminium would remove the carbon monoxide by reacting with it, forming a mixture of alumina and aluminium carbide, thus: $6Al + 3CO = Al_4C_3 + Al_2O_3$.

This seems to have taken place, for the aluminium was found to have been largely converted into carbide, and in the condenser tube were found 2 grams of magnesium as powder and a further quantity of 2 grams which had been melted in the hot tube and had run down to the bottom, where it solidified. This metal gave on analysis Mg = 99·45, Al = 0·47 per cent. If the addition of the aluminium was omitted, it was found that in place of the fused metal there was a mixture of magnesia and carbon, formed doubtless by the action of carbon monoxide on the molten metal. Some powder found in the tube, however, was shown to consist largely of metal, for it gave a mixture of hydrogen, acetylene, and hydrogen sulphide on treatment with dilute acid.

When the carbon monoxide was absorbed by aluminium, it was possible for the magnesium formed to run together; without the aluminium, however, this metal was oxidised by the carbon monoxide.

Conclusion.

The work here recorded seems to prove satisfactorily that magnesia is reduced by carbon, not only at the high temperature of the electric arc, but as low as 1700°.

Watts (*Trans. Amer. Electrochem. Soc.*, 1907, **11**, 279) mentions the fact that carbon can be volatilised from a bed of magnesia, and he obtained sublimates consisting of intimate mixtures of magnesium oxide and carbon; his explanation of the reaction is similar to that put forward here, although he was unable to produce evidence of the existence of free metal.

The present work, however, shows clearly that the metal can be isolated, although under ordinary conditions re-oxidation of the magnesium is effected by the carbon monoxide, for if some device is used for removing this gas, for instance, by working in a vacuum, by absorption of aluminium, or by a rapid stream of hydrogen, then metallic magnesium is obtained. The condensed magnesium is always associated with small quantities of a carbide, which, on treatment with water or dilute acid, gives off acetylene. Small quantities of this carbide are also found together with the mixture of magnesia and carbon in the condensate obtained when magnesia and carbon are heated together in an open furnace. All attempts to prepare this carbide from magnesium and carbon in anything like a pure state failed, but it was shown only to give off acetylene on treatment with dilute acid. It is therefore probably identical with Berthelot's carbide, prepared by heating magnesium to a red heat in a stream of acetylene. In this case, it must be formed by the cooling magnesium coming into contact with acetylene, which is always present in traces where carbon and hydrogen come together at temperatures of 1700° and upwards (Pring and Hutton, Trans., 1906, **89**, 1600).

In all furnaces, unless very exceptional precautions be taken, there is a considerable amount of hydrogen present due to the decomposition of moisture. In no case was any carbide found in the hot parts of the furnace. This confirms the suggestion that it is identical with Berthelot's carbide, for Moissan showed that the latter was decomposed at high temperatures.

Finally, I wish to thank Dr. R. S. Hutton for many valuable suggestions, and for the interest he has taken in the work.

ELECTRO-CHEMICAL LABORATORY,
THE UNIVERSITY,
MANCHESTER.

XXXII.—*Constitution and Colour of Azo-compounds. Part II. The Salts of Parahydroxyazo-compounds with Acids.*

By JOHN JACOB FOX and JOHN THEODORE HEWITT.

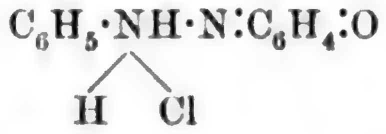
SOME fourteen years ago (*Ber.*, 1893, **26**, 2975) one of the authors of the present communication observed that ortho- and meta-chlorobenzeneazophenols could apparently each exist in two different modifications; these were subsequently found not to be isomeric as was at first supposed, but to differ from one another by half a molecule of water (*Ber.*, 1895, **28**, 799). The colour change was so striking when the hydrated form was converted into the anhydrous substance that it seemed improbable such a difference was merely due to loss of water of crystallisation, and further examination appeared desirable. From hot alcoholic solutions, *m*-chlorobenzeneazophenol separates in brilliant yellow crystals which are anhydrous; when water is added to a cold alcoholic solution, chocolate coloured crystals of the formula

$$(C_{12}H_9ON_2Cl)_2,H_2O$$

are usually deposited. On endeavouring to find out the exact conditions under which the two forms might be obtained, it soon became apparent that the hydrated form was generally, although not necessarily, produced in presence of a small amount of free mineral acid. Hewitt and Pope (*Ber.*, 1897, **30**, 1624) then found that many azophenols formed hydrates when first finely ground with concentrated hydrochloric acid and then washed with water, and it was very noticeable that dark coloured compounds were obtained by the action of hydrochloric acid on azophenols.

Salts of azo-compounds with mineral acids had been noticed by several experimenters;* Hewitt and Pope observed, however, that the hydrochlorides could be obtained in a pure condition by leading dry hydrogen chloride into benzene solutions of the azophenols and these contained one molecular proportion of hydrogen chloride per molecule of azo-compound. Since similar compounds were not isolated from the corresponding ethyl ethers, the idea occurred that the salts were derived from quinonehydrazones. Professor P. Jacobson pointed out to the authors that W. Fischer, working under his direction, had found that benzeneazophenetole was far more soluble in concentrated hydrochloric acid than the parent azophenol, and, whilst a hydrochloride was not isolated, a platinichloride had been obtained and analysed. Further, Professor Jacobson had the great kindness to place a number of dissertations carried out under his guidance at the authors' disposal, who confirmed the results contained therein and studied the relationships of these hydrochlorides to the hydrates.

The existence of salts of the ethyl ethers with mineral acids caused the idea of a quinonehydrazone formula for the salts to be temporarily abandoned; Farmer and Hantzsch, however, definitely adopted the formula



$$C_6H_5\cdot\underset{H\qquad Cl}{NH\cdot N}{:}C_6H_4{:}O$$

in 1899 (*Ber.*, 1899, **32**, 3091), and when Hewitt obtained a fair yield of benzeneazo-*o*-nitrophenol by the action of warm dilute nitric acid on benzeneazophenol (Trans., 1900, **77**, 99) whereas Noelting obtained *p*-nitrobenzeneazophenol when nitration was effected in concentrated sulphuric acid solution (*Ber.*, 1887, **20**, 2997) a radical difference in the constitution of the salts and the azophenols was evident, the azophenols being regarded as hydroxylic compounds, the salts possessing the constitution which Farmer and Hantzsch had adopted. In this view Auwers concurred (*Ber.*, 1900, **33**, 1302), and the salts seem to have been accepted by many as quinonehydrazone derivatives, although Jacobson records the fact that hydroxyazobenzene also forms salts with mineral acids (*Ber.*, 1903, **36**, 4107).

---

* The literature is referred to by Hewitt and Pope (*loc. cit.*).

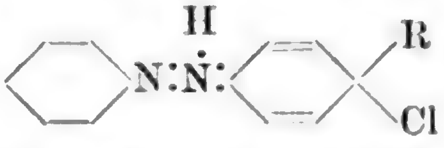
Last year W. B. Tuck examined the absorption spectra of benzeneazophenol and benzeneazophenetole in alcoholic and concentrated hydrochloric acid solution, finding that solutions of these substances in the same solvent exhibited similar absorptions. Since benzeneazophenetole undoubtedly possesses the constitution

$$C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}O{\cdot}C_2H_5,$$

benzeneazophenol is regarded by Tuck as having a hydroxyazo-structure, and Tuck further deduces from the similarity of the absorptions of the two substances in hydrochloric acid that "this undoubtedly proves that the hydrochlorides of both the free *p*-hydroxyazo-compounds and of the ethers have similar structures, and consequently the hydrochlorides of the free hydroxyl substances have an azo-structure."

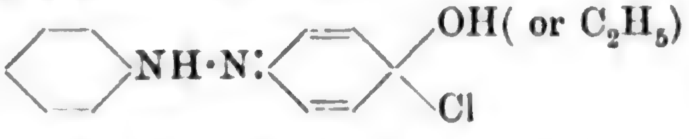
If this conclusion of Tuck's be granted, it is impossible to understand the difference in the behaviour of hydroxyazo-compounds to substituting agents according to whether the free azophenol or a salt with a mineral acid were employed; if the phenol group remains phenolic, then substitution must necessarily first take place in that group.

F. Baker has more recently suggested a carbonium formula for the salts (Trans., 1907, **91**, 1500), but grave objections may be urged against a structure which involves nitrogen in a quinquevalent condition never before observed. Baker actually writes the general formula as



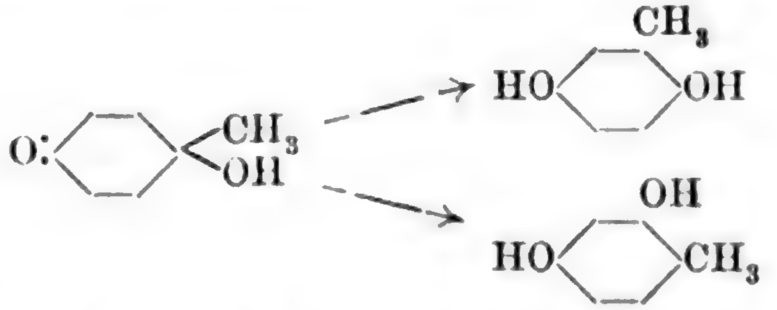
.

If in this formula, $R = OH$ or $O{\cdot}C_2H_5$, there is no apparent reason why the benzene nucleus should be so easily attacked by substituting agents, although in a modified form,

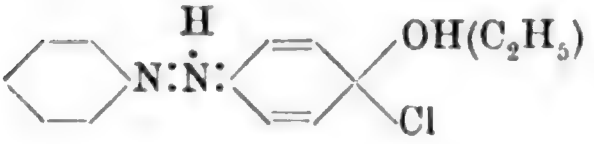


,

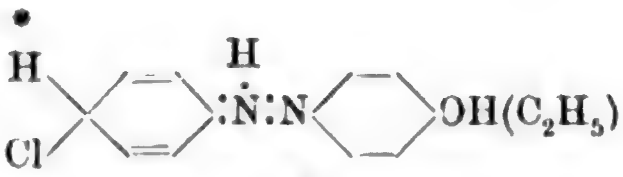
this objection as well as the other one regarding the valency of the nitrogen would disappear. Such a formula may have some value, although one would expect substances of this type readily to undergo isomeric change in a manner similar to that exhibited by the analogously constituted "chinols" discovered by Bamberger (*Ber.*, 1900, **33**, 3600).



Whether Baker intends to represent the hydrochloride of benzeneazophenol by *A* or *B*



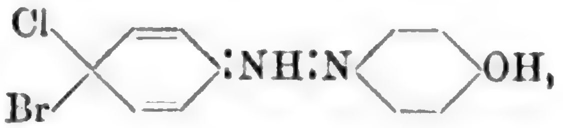
A.



B.

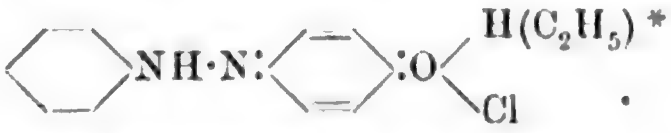
is not apparent, for despite the general formula shown in his paper, in which the meaning attached to R is not stated (*loc. cit.*), in reading his communication to the Society he remarked that a hydrogen atom such as that marked with an asterisk in formula *B* would be peculiarly liable to substitution. The objections which may be raised to formula *A* have already been stated, against *B* may be urged the same objections and others in addition. In the first place the phenolic group remains phenolic and should be peculiarly liable to attack (quite at variance with the facts), secondly the observation made by Grandmougin and Guisan (*Ber.*, 1907, **40**, 4205) that *p*-tolueneazosalicylic acid when dissolved in concentrated sulphuric acid is nitrated in the ortho-position with respect to the azo-group in the toluene nucleus. Further, benzeneazo-*a*-naphthol and its *p*-nitro-derivative both give yellow solutions in neutral solvents but purple solutions (absorption in the yellow and green) in concentrated hydrochloric acid, so that it may be assumed that the salts formed with acids are of the same type. The idea of a salt containing such a group as $\genfrac{}{}{0pt}{}{NO_2}{Cl}\!\!>\!C\!<$ (required by formula *B*) scarcely seems feasible, but if it be argued that such a grouping may be quite stable, then surely a dimethylamino-group must have an opposite effect. To test the point, *p*-dimethylaminobenzeneazo-*a*-naphthol was prepared; its solutions in alkalis, neutral solvents, or dilute acids are yellow, but in concentrated hydrochloric acid the solution is purple and yields on concentration a hydrochloride which contains two molecular proportions of hydrogen chloride to one of the azo-compounds. Formula *B* requires in this case the grouping $\genfrac{}{}{0pt}{}{ClH(CH_3)_2N}{Cl}\!\!>\!C\!<$, and it would certainly be remarkable if this grouping as well as the groupings $\overset{H}{\underset{Cl}{}}{>}C{<}$ and $\overset{NO_2}{\underset{Cl}{}}{>}C{<}$ were not merely possible but also exhibited about the same degree of stability and the same behaviour as salts.

The most decisive evidence against the formula *B* is furnished by the fact that the hydrochloride of *p*-bromobenzeneazophenol and the hydrobromide of *p*-chlorobenzeneazophenol are absolutely different substances regenerating their components on hydrolysis, whereas the formula *B* requires the same substance,



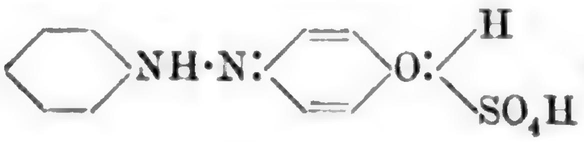
for both. Tschitschibabin has employed a similar method with regard to the coloured salts of triphenylcarbinol (*Ber.*, 1907, **40**, 3965).

The structures discussed being unsatisfactory, some other constitution has to be found for the salts, which will recognise the similarity in constitution of the hydrochlorides of the hydroxyazo-compounds and their ethyl ethers, and this may be arrived at by regarding the compounds with mineral acids as oxonium salts; for example,

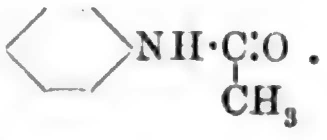


Not only does this formula agree with the facts stated, but it goes further in that it necessitates in each case a longer chain of alternate double and single linkings for the salts, which, as shown by Hewitt and Mitchell for the alkali salts of *p*-nitroazophenols, accompanies the shifting of the absorption to the red end of the spectrum.

It also agrees with the nitration in concentrated sulphuric acid, the benzene nucleus in acetanilide and in the sulphate of benzeneazophenol being in analogous states.



and

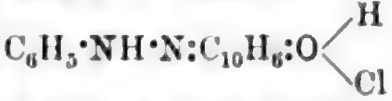
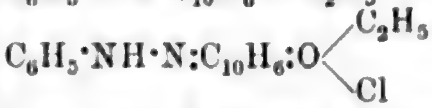
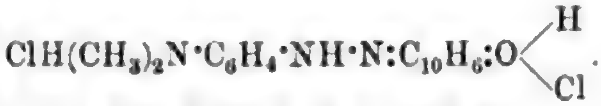
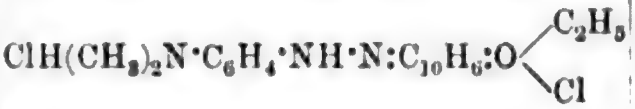
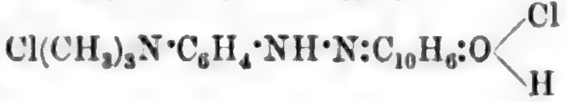


In fact, the ortho-para law of substitution is obeyed, whilst aromatic sulphates in presence of an excess of concentrated sulphuric acid nitrate frequently in the meta-position.

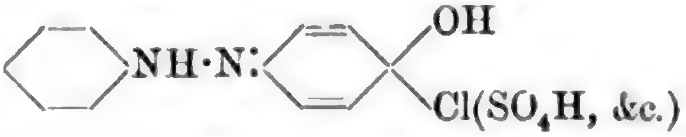
The following constitutions are therefore assigned to the substances which have been examined:

---

* During the passage of this communication through the press, Professor Grandmougin has sent me a copy of Dr. Guisan's dissertation in which the oxonium formula for the salts is advocated. (*Contribution à l'étude des dérivés azoïques de l'acide salicylique*, p. 71, Zürich, 1907.)—J. T. H.

Substance.	Formula.	Absorption.
Benzeneazo-*α*-naphthol	$C_6H_5\cdot N:N\cdot C_{10}H_6\cdot OH$	Blue and violet
,, ,, hydrochloride	 $C_6H_5\cdot NH\cdot N:C_{10}H_6:O\genfrac{}{}{0pt}{}{H}{Cl}$	Yellow and green
Benzeneazo-*α*-naphthyl ethyl ether	$C_6H_5\cdot N:N\cdot C_{10}H_6\cdot O\cdot C_2H_5$	Blue and violet
Benzeneazo-*α*-naphthyl ethyl ether hydrochloride	 $C_6H_5\cdot NH\cdot N:C_{10}H_6:O\genfrac{}{}{0pt}{}{C_2H_5}{Cl}$	Yellow and green
Dimethylaminobenzeneazo-*α*-naphthol	$(CH_3)_2N\cdot C_6H_4\cdot N:N\cdot C_{10}H_6\cdot OH$	Blue and violet
Dimethylaminobenzeneazo-*α*-naphthol monohydrochloride	$ClH(CH_3)_2N\cdot C_6H_4\cdot N:N\cdot C_{10}H_6\cdot OH$	Blue and violet
Dimethylaminobenzeneazo-*α*-naphthol dihydrochloride	 $ClH(CH_3)_2N\cdot C_6H_4\cdot NH\cdot N:C_{10}H_6:O\genfrac{}{}{0pt}{}{H}{Cl}$ ...	Yellow and green
Dimethylaminobenzeneazo-*α*-naphthyl ethyl ether......	$(CH_3)_2N\cdot C_6H_4\cdot N:N\cdot C_{10}H_6\cdot O\cdot C_2H_5$	Blue and violet
Dimethylaminobenzeneazo-*α*-naphthyl ethyl ether monohydrochloride	$ClH(CH_3)_2N\cdot C_6H_4\cdot N:N\cdot C_{10}H_6\cdot O\cdot C_2H_5$ ...	Blue and violet
Dimethylaminobenzeneazo-*α*-naphthyl ethyl ether dihydrochloride	 $ClH(CH_3)_2N\cdot C_6H_4\cdot NH\cdot N:C_{10}H_6:O\genfrac{}{}{0pt}{}{C_2H_5}{Cl}$	Yellow and green
Dimethylaminobenzeneazo-*α*-naphthol methiodide......	$I(CH_3)_3N\cdot C_6H_4\cdot N:N\cdot C_{10}H_6\cdot OH$	Blue and violet
Dimethylaminobenzeneazo-*α*-naphthol methochloride hydrochloride	 $Cl(CH_3)_3N\cdot C_6H_4\cdot NH\cdot N:C_{10}H_6:O\genfrac{}{}{0pt}{}{Cl}{H}$ ...	Yellow and green

It will not escape attention that the formula



is not definitely negatived, but the fact that isomerisation analogous to the transformation of the "chinols" does not take place, renders it extremely improbable.

It may be added that if the formula advocated in this paper for the salts formed by azophenols with mineral acids is correct, the hydrates containing one molecule of water are the corresponding pseudobases, $Ar\cdot NH\cdot N:C_6H_4(OH)_2$. Farmer and Hantzsch assign the same structure to these "abnormal hydrates" from a different line of reasoning (*loc. cit.*). The hydrates containing only one molecule of water to two molecules of the azophenol must then be anhydrides of these pseudo-bases and possess the constitution

$$[Ar\cdot NH\cdot N:C_6H_4(OH)\cdot]_2O.$$

Such anhydride formation from pseudo-bases has been occasionally observed in the case of other compounds (for example, Werner, *Ber.*, 1901, **34**, 3305).

EXPERIMENTAL.

The hydrochlorides of benzeneazophenol and its ethyl ether have already been shown by Tuck (*loc. cit.*, pp. 450, 451) to possess similar absorption spectra, and he draws the conclusion that they are similarly constituted. The same relationship is observed in the case of benzeneazo-α-naphthol and its ethyl ether when dissolved in hydrochloric acid; the observations recorded in this paper refer only to the visible part of the spectrum. With a layer 4 mm. in thickness we observed for an alcoholic $N/1,000$ solution of benzeneazo-α-naphthol a transmission of the visible spectrum as far as wave length 540 $\mu\mu$, an equimolecular solution of the ethyl ether transmitting as far as 510 $\mu\mu$. The effect of forming the sodium salt is similar to that observed by Tuck for benzeneazophenol, light not passing through beyond 582 $\mu\mu$ at the same dilution. But solutions of the azonaphthol and its ethyl ether in concentrated sulphuric acid are violet, the absorption being characterised by a strong and persistent band in the yellow and green, the limits of which in $N/10,000$ solution were observed as 600—525 $\mu\mu$ for the azonaphthol and 600—535 $\mu\mu$ for its ethyl ether. The ethyl ether exhibits the same band in strong hydrochloric acid solution, the edges being shifted slightly towards the violet end of the spectrum (590—525 $\mu\mu$); we considered it as well to examine the absorption in both acids, as very frequently sulphuric acid is a more convenient solvent. Evidently the replacement of one acid by another has no very marked effect.

In the case of *p*-nitrobenzeneazo-α-naphthol (Meldola, Trans., 1885, **47**, 661) the free azo-compound in neutral solvents screens the violet end of the spectrum in quite the same manner as the unsubstituted compound, but on adding alkali to the solution a band is formed in the yellow and green, and the red and blue ends of the spectrum are transmitted. One also finds a persistent absorption band when the azonaphthol is dissolved in concentrated sulphuric or hydrochloric acids. The head of the band in concentrated hydrochloric acid lies about 600 $\mu\mu$; the band in alkaline solution is near this, but much broader.

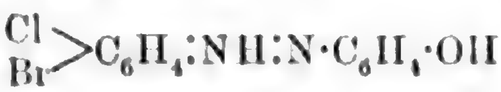
In the case of dimethylaminobenzeneazo-α-naphthol one has to deal with the spectra of alkaline, neutral, dilute acid, and strongly acid solutions. The absorption of the neutral solution is very similar to that of the unsubstituted benzeneazo-α-naphthol; the yellow solution in dilute hydrochloric acid which contains the monohydrochloride differs in that the absorption begins slightly nearer the violet end of the spectrum and the edge of the band is rendered much sharper. When, however, the azo-compound is dissolved in concentrated hydrochloric acid the spectrum changes entirely, and a band appears in the yellow and green the head of which is about 600 $\mu\mu$. From such a solution a dihydrochloride is deposited on concentration.

The methiodide and *O*-ethyl ether of dimethylaminobenzeneazo-α-naphthol show quite analogous colour changes with variation in the concentration of acid.

It has been stated in the introduction that the hydrochloride of *p*-bromobenzeneazophenol and the hydrobromide of *p*-chlorobenzeneazophenol are different substances. The first of these salts was described by Hewitt, Moore, and Pitt (*Ber.*, 1898, **31**, 2116), who precipitated a benzene solution of the azophenol with dry hydrogen chloride; they described the *p*-bromobenzeneazophenol as melting at 157°. A redetermination of the melting point of their original specimen showed that the substance softened at 154° and melted completely at 158° (uncorr.). A recrystallisation of the specimen from dilute alcohol raised the melting point to 158·5° (162° corr.). Hewitt, Moore, and Pitt record 154° for the melting point of *p*-chlorobenzeneazophenol, a redetermination gave 153·5° (157° corr.).

p-Bromobenzeneazophenol was ground up very finely with concentrated hydrochloric acid, the resulting red, crystalline paste spread on a porous tile and dried in the air for several days. The *p*-chlorobenzeneazophenol was treated in a similar manner with concentrated hydrobromic acid. The result of the exposure was that each salt when decomposed into its components contained less than one molecular proportion of acid per molecule of azophenol, in the circumstances a matter of no moment as the analyses of many salts have been published. The decomposition was effected by covering the salt with water, warming, and gradually adding *N*/10 solution of potassium hydroxide until the azophenol was dissolved. The azophenol was then precipitated by dilute acetic acid, collected, and washed; to the filtrate a few drops of nitric acid were added, and then silver nitrate in slight excess. The silver halide so precipitated was collected, washed with water and alcohol, and dried. In this way an azophenol was obtained from the hydrochloride of *p*-bromobenzeneazophenol which melted at 158—159° (uncorr.), and which did not depress the melting point of pure *p*-bromobenzeneazophenol. The silver halide contained Ag = 75·06; AgCl requires Ag = 75·28 per cent.

The azophenol recovered from *p*-chlorobenzeneazophenol hydrobromide melted at 153·5° (uncorr.), whether alone or mixed with *p*-chlorobenzeneazophenol. The silver halide obtained from this salt contained Ag = 57·49; AgBr requires Ag = 57·44 per cent. Hence there is no doubt that the formula



$$\begin{matrix}\mathrm{Cl}\\\mathrm{Br}\end{matrix}\!\!>C_6H_4{:}NH{:}N{\cdot}C_6H_4{\cdot}OH$$

for both these salts is out of the question.

That no change analogous to the isomerisation of "chinols" to quinol or resorcinol derivatives had taken place renders the formulæ

$$(Br)Cl\cdot C_6H_4\cdot N\colon NH\colon C_6H_4{<}\substack{OH \\ Br(Cl)}$$

and

$$(Br)Cl\cdot C_6H_4\cdot NH\cdot N\colon C_6H_4{<}\substack{OH \\ Br(Cl)}$$

very improbable. It cannot be urged that two or three days was too short a time to wait for the change to take place, since it was found that the original specimen prepared by Moore and Pitt in 1898 had, owing to being preserved in a corked specimen tube, lost practically all its hydrochloric acid and now melted at 157° (uncorr.), its melting point not being depressed when mixed with *p*-bromobenzeneazophenol.

Dimethylaminobenzeneazo-α-naphthol, $(CH_3)_2N\cdot C_6H_4\cdot N\colon N\cdot C_{10}H_6\cdot OH$.

A solution of 6·8 grams of *p*-phenylenedimethyldiamine (or the equivalent amount of sulphate) in 30 c.c. water and 11 grams of concentrated hydrochloric acid was well cooled and diazotised with 3·5 grams of sodium nitrite dissolved in a small quantity of water. During the process of diazotisation rather remarkable colour changes (red to green) were observed, and the solution was then poured into a well-cooled alkaline solution containing 7·2 grams of α-naphthol. The solution immediately became dark red, but the process of combining was allowed to proceed overnight. To liberate the azonaphthol a stream of carbon dioxide was found to give the best results, and the precipitate after collection, washing with water and drying, approximated to the weight required by theory. From the dried mass impurities were removed by treatment with repeated quantities of cold benzene; the residue gave a brown solution with nearly all the usual organic solvents. For analysis the substance was crystallised from chloroform; it separated in small, dark chocolate coloured needles. The substance decomposes on heating at 159° (uncorr., ordinary rate of heating). It dissolves in dilute acids with a yellow or brown shade; the colour in strong acids is violet or purple:

0·1271 gave 0·3450 CO_2 and 0·0674 H_2O. C = 74·04; H = 5·93.
0·1351 „ 0·3664 CO_2 „ 0·0720 H_2O. C = 74·00; H = 5·96.
0·1672 „ 20·5 c.c. N(over KOH) at 17° and 757 mm. N = 14·28.
$C_{18}H_{17}ON_3$ requires C = 74·22; H = 5·88; N = 14·43 per cent.

Monohydrochloride.—The preceding substance, in virtue of its dimethylamino-group, dissolves easily in dilute hydrochloric acid with a brown colour. The salt thus formed separates in needles, which exhibit a metallic reflex after drying:

0·1782 gave 0·0798 AgCl. Cl = 11·07.

$C_{18}H_{18}ON_3Cl$ requires Cl = 10·84 per cent.

Dihydrochloride.—This salt is readily prepared by dissolving the base in benzene or chloroform, and leading dried hydrogen chloride into the solution. The very dark purple precipitate is collected, washed with benzene, and dried in the air:

0·1778 gave 0·1438 AgCl. Cl = 20·00.

$C_{18}H_{19}ON_3Cl_2$ requires Cl = 19·50 per cent.

Platinichloride.—The platinichloride, as obtained by evaporating the azonaphthol with a solution of platinic chloride in concentrated hydrochloric acid, separates in a crystalline condition, and after filtering may be washed with alcohol before drying; it is the salt of a diacid base:

0·2113 gave 0·0594 Pt. Pt = 28·11.
0·1782 „ 0.0498 Pt. Pt = 27·95.

$C_{18}H_{17}ON_3,H_2PtCl_6$ requires Pt = 27·82 per cent.

Methiodide.—The base is dissolved in methyl alcohol, the calculated amount of methyl iodide added, and allowed to stand several days. Small, almost black, prisms separate; the solutions of this salt in neutral solvents are brown, but in concentrated acids a purple colour is developed:

0·1358 gave 0·0732 AgI. I = 29·13.

$C_{19}H_{20}ON_3I$ requires I = 29·34 per cent.

Acetyl derivative.—$(CH_3)_2N\cdot C_6H_4\cdot N{:}N\cdot C_{10}H_6\cdot O\cdot CO\cdot CH_3$.

The acetyl derivative was prepared in the usual manner by boiling with acetic anhydride and fused sodium acetate. The excess of acetic anhydride was removed by pouring into alcohol, and the acetylated base precipitated by the addition of ammonia. The substance is soluble in the usual organic solvents with a brown shade; for analysis it was purified by repeated precipitations with light petroleum from its solution in chloroform. The red crystalline powder thus obtained melted at 245—247° (uncorr.), and gave the following result on analysis:

0·1444 gave 0·3798 CO_2 and 0·0730 H_2O. C = 71·73; H = 5·65.

$C_{20}H_{19}O_2N_3$ requires C = 72·07; H = 5·70 per cent.

Benzoyl derivative.—The benzoyl derivative was prepared by the Schotten-Baumann method, and purified by repeated precipitation with light petroleum from its solution in chloroform. Its colour in the solid condition is also red: it may be noted that both acetyl and benzoyl derivatives have a distinctly lighter shade than the parent azonaphthol. The substance melted at 190° (uncorr.) with decomposition, slight softening taking place at 183°

0·1430 gave 0·3958 CO_2 and 0·0864 H_2O. C = 75·56 ; H = 5·35.

$C_{25}H_{21}O_2N_3$ requires C = 75·95 ; H = 5·32 per cent.

Dimethylaminobenzeneazo-a-naphthyl ethyl ether.—The azonaphthol was dissolved in the calculated quantity of dilute sodium hydroxide solution, and boiled under reflux for several hours * with one molecular proportion of diethyl sulphate. The ethylated base separated as a precipitate; after collection, digestion with dilute sodium hydroxide solution and washing, it was crystallised from chloroform, being obtained in small dark prisms, melting with decomposition at 216° (uncorr.):

0·1028 gave 0·2826 CO_2 and 0·0636 H_2O. C = 75·00 ; H = 6·82.

$C_{20}H_{21}ON_3$ requires C = 75·24 ; H = 6·59 per cent.

Dihydrochloride.—The violet solution of the azonaphthol in concentrated hydrochloric acid deposited nearly black needles in concentration; these, after collection and air-drying, proved to be the dihydrochloride, analysis of two preparations giving the following results:

0·1358 gave 0·1026 AgCl. Cl = 18·66.
0·1352 „ 0·1016 AgCl. Cl = 18·59.

$C_{20}H_{23}ON_3Cl_2$ requires Cl = 18·12 per cent.

Platinichlorides.—Two platinichlorides were prepared showing that the base can exercise monacid or diacid functions. By adding a solution of the base in dilute hydrochloric acid to alcoholic platinic chloride a brown precipitate was obtained, which proved to be the compound of two molecules of the base with one molecule of hydrogen platinichloride:

0·1512 gave 0·0278 Pt. Pt = 18·32.

$(C_{20}H_{21}ON_3)_2,H_2PtCl_6$ requires Pt = 18·60 per cent.

The other salt was obtained by evaporating a solution of the base in concentrated hydrochloric acid with platinic chloride; it separated in nearly black needles:

0·1062 gave 0·0282 Pt. Pt. = 26·55.

$C_{20}H_{21}ON_3,H_2PtCl_6$ requires Pt = 26·75 per cent.

Finally, it is our pleasant duty to record our sincere thanks to the Badische Anilin- und Soda-Fabrik, and especially to Mr. H. Zilz, for their kindness in placing a considerable quantity of *p*-phenylenedimethyldiamine sulphate at our disposal, and to Mr. R. H. Fleming for aid in the experimental work.

EAST LONDON COLLEGE.

---

* The prolonged heating is probably unnecessary.

XXXIII.—*The Influence of Foreign Substances on Transition Temperatures and the Determination of Molecular Weights.*

By HARRY MEDFORTH DAWSON and COLIN GYRTH JACKSON.

THE object of this paper is to record the results of experiments made to determine the depression of certain so-called transition temperatures on the addition of foreign substances soluble in the liquid which is formed at the temperature of transition.

The systems involved in such transition phenomena are more complex than those which are met with in the application of the freezing-point method of determining molecular weights. Whereas, in the case of the freezing point, the temperature constancy is determined by the co-existence in equilibrium of a solid and a liquid phase of the same composition, two or more solid phases are in equilibrium with a liquid phase, the composition of which bears, in general, no simple relationship to that of the solid phases, when a transition phenomenon of the type investigated in this paper is in question. If the change is the dehydration of a hydrated substance, two solid phases participate in the equilibrium corresponding with the transition temperature; if it is the formation of a double salt from two simple salts or the decomposition of a double salt into its component simple salts with loss of water, the number of such solid phases is three. Apart from this difference in the number of the solid phases which participate in the equilibrium and the absence of any simple relationship between the composition of the liquid phase and that of the solid phases, there is, however, no essential distinction between true freezing points and transition points of the type referred to. The practical constancy of such transition temperatures has been clearly demonstrated by Richards and Churchill (*Zeitsch. physikal. Chem.*, 1898, **26**, 690), who found the temperature at which sodium sulphate decahydrate is transformed into the anhydrous salt to be 32·379° (hydrogen scale). Richards and Wells (*Zeitsch. physikal. Chem.*, 1906, **56**, 348) found similarly that the transformation of sodium bromide dihydrate into the anhydrous salt takes place at 50·674° (hydrogen scale). Such temperatures have been suggested as suitable fixed points for thermometric purposes (compare also Meyerhoffer and Saunders, *Zeitsch. physikal. Chem.*, 1898, **27**, 367; Richards and Churchill, *ibid.*, 1898, **28**, 313).

The depression of the temperature, at which sodium sulphate decahydrate is transformed into the anhydrous salt and a solution saturated with regard to this substance, on the addition of foreign soluble substances, was investigated by Löwenherz (*Zeitsch. physikal. Chem.*, 1895, **18**, 70). A constant representing the molecular lowering of the transition temperature was calculated, and by using various non-electrolytes—carbamide, glycocoll, dextrose, formamide, and glycerol—it was found that molecular weight values in close agreement with theory are obtained when the molecular depression of the transition temperature is taken as 32·6.

This is the numerical value obtained for the constant when the concentration of the foreign substance present is referred to 100 grams of the decahydrate. Since the lowering of the transition temperature is determined solely by the concentration of the foreign substance in the solution formed at this temperature, it may be doubted whether this is the most convenient way of evaluating the constant. In the authors' opinion, the referring of the concentration to 100 grams of the solution in which the foreign substance is contained is a more convenient and correct procedure. The relationship between the two constants, calculated in these different ways, is determined by the equation which expresses the change taking place at the transition temperature in terms of the composition of the solution formed. Since 100 parts of this solution contain 33·34 parts of Na_2SO_4, this equation may be written: $Na_2SO_4,10H_2O = 0{\cdot}367Na_2SO_4 + 0{\cdot}100(100H_2O,6{\cdot}33NaSO_4)$.

From this, it follows that 100 parts of the decahydrate yield 87·3 parts of solution, and the molecular lowering of the transition temperature, when the concentration of the dissolved substance is referred to 100 grams of the saturated solution, is $32{\cdot}6 \times \frac{87{\cdot}3}{100} = 28{\cdot}5$.

Van't Hoff and Dawson (*Zeitsch. physikal. Chem.*, 1897, **22**, 598) examined the influence of foreign substances on the temperature (116·67°, according to van't Hoff and Meyerhoffer, *ibid.*, 1898, **27**, 81) at which magnesium chloride hexahydrate is converted into the tetrahydrate according to the equation:

$$MgCl_2,6H_2O = 0{\cdot}0795MgCl_2,4H_2O + 0{\cdot}0568(100H_2O,16{\cdot}2MgCl_2),$$

and found similar regularities, the value of the molecular lowering of the transition temperature referred to 100 grams of the solution being 76.

The temperature (40·41°), at which rubidium racemate,

$$(Rb_2C_4H_4O_6)_2,4H_2O,$$

is converted into a mixture of the anhydrous *d*- and *l*-tartrates, was found by van't Hoff and Müller (*Ber.*, 1898, **31**, 2206) to be depressed on the addition of rubidium carbonate. The molecular lowering, referred to 100 grams of rubidium racemate, was calculated to be 100. Since the saturated solution at the transition temperature contains 13·48 molecules of tartrate per 100 molecules of water, the change taking place may be written:

$$(Rb_2C_4H_4O_6)_2,4H_2O = 0{\cdot}73d\text{-}Rb_2C_4H_4O_6 + 0{\cdot}73l\text{-}Rb_2C_4H_4O_6 + 0{\cdot}040(100H_2O,13{\cdot}48Rb_2C_4H_4O_6).$$

According to this, 100 parts of racemate yield 34·4 parts of solution, and the molecular lowering of the transition temperature referred to 100 grams of the solution is therefore $108 \times \frac{34{\cdot}4}{100} = 37{\cdot}1$.

So far as the authors are aware, these isolated observations are the only ones relating to the depression of transition temperatures by foreign substances, which can be utilised for the evaluation of constants for the purpose of molecular weight determinations.

In the experiments recorded in this paper, three further changes have been investigated and constants which represent the molecular lowering of the temperature of transition have been calculated.

The apparatus used was similar to that described by Meyerhoffer (*Zeitsch. physikal. Chem.*, 1897, **22**, 619), effective mixing of the reacting phases being achieved by means of a rapidly rotating perforated cylindrical stirrer surrounding the Beckmann thermometer on which the temperature readings were made. By means of a small electric motor with an easily adjustable resistance in circuit, the stirrer could be made to revolve with any desired rapidity and the rate of rotation maintained practically constant throughout each experiment. During the period of supercooling and subsequent rise of temperature, the tube containing the reaction mixture was surrounded by a wider glass tube, which was immersed in a regulated water thermostat having a temperature a few degrees below the transition temperature under investigation. As a readily soluble foreign substance, carbamide was used to depress the investigated transition temperatures.

Transformation of Sodium Thiosulphate Primary Pentahydrate into Primary Dihydrate.—At about 48°, sodium thiosulphate primary pentahydrate loses 3 molecules of water and yields the corresponding dihydrate (compare Young and Burke, *J. Amer. Chem. Soc.*, 1906, **28**, 315) together with a solution which at the transition temperature contains 159·8 parts of sodium thiosulphate per 100 parts of water. Corresponding with this, the change taking place may be represented by the equation: $Na_2S_2O_3,5H_2O = 0{\cdot}14Na_2S_2O_3,2H_2O +$

$$0{\cdot}0472(100H_2O,18{\cdot}20Na_2S_2O_3).$$

From this equation, the quantity of solution yielded by a given weight of sodium thiosulphate of determined conposition can be readily calculated.

From 65 to 100 grams of recrystallised thiosulphate were used in each experiment, the temperature being maintained at 55—60° until the primary pentahydrate had completely disappeared. When the system had been supercooled to the extent of about 0·5°, a crystal of the primary pentahydrate was added. In order to prevent surface evaporation, the partly fused mass was in some cases covered with a layer of heavy petroleum, but this was not found to have any definite influence on the results obtained. Table I contains the recorded experimental data, the composition of the thiosulphate used being indicated in the first column :

TABLE I.

Composition of thiosulphate.	Weight of thiosulphate in grams.	Weight of carbamide in grams.	Observed lowering of temperature.	Molecular lowering.
$Na_2S_2O_3,5{\cdot}007\ H_2O$	65·4	0·4425	0·554°	43·7
$Na_2S_2O_3,5{\cdot}03\ H_2O$	90·06	0·7195	0·640	43·1
$Na_2S_2O_3,5{\cdot}007\ H_2O$	65·6	0·6940	0·857	43·3
$Na_2S_2O_3,5{\cdot}03\ H_2O$	102·5	1·4055	1·072	42·1
$Na_2S_2O_3,5{\cdot}03\ H_2O$	90·06	1·2605	1·095	42·1
			Mean.........	42·9

Referred to 100 grams of the saturated transition solution, the depression of the transition temperature is therefore 43° per gram-molecule of foreign substance present.

Transformation of Sodium Bromide Dihydrate into Anhydrous Sodium Bromide.—The saturated solution at the temperature of transition (50·7°) contains 117·4 parts of sodium bromide per 100 parts of water. The change which occurs at this temperature may therefore be represented by the equation :

$$NaBr,2H_2O = 0{\cdot}589NaBr + 0{\cdot}02(100H_2O,20{\cdot}54NaBr),$$

according to which 100 grams of the dihydrate yield 56·36 grams of the saturated solution.

About 100 grams of sodium bromide ($NaBr,0{\cdot}035H_2O$) and 35 grams of water were heated at about 60° with vigorous stirring of the contents of the tube until a saturated solution of the anhydrous salt was obtained. The system was then allowed to cool in the air until the transition temperature was approximately reached, when the tube was placed in its outer jacket immersed in a thermostat at a temperature of 43—45°. Table II contains the experimental data :

TABLE II.

Weight of bromide in grams.	Weight of water in grams.	Weight of carbamide in grams.	Observed lowering of temperature.	Molecular lowering.
101·7	34·66	0·4905	0·370°	34·7
103·0	36·20	0·5685	0·415	35·1
101·7	34·66	0·908	0·680	34·5
103·0	36·20	1·0535	0·738	33·7
			Mean.........	34·5

Referred to 100 grams of the transition solution, one gram-molecule of foreign substance depresses the transition temperature 34·5°.

Formation of Tachhydrite from Calcium and Magnesium Chloride Hexahydrates.—When the hexahydrates of calcium and magnesium chloride are intimately mixed and gently warmed, the two simple salts react to form the double salt tachhydrite, $CaCl_2,2MgCl_2,12H_2O$. Taking into account the composition of the saturated solution which is formed at the transition temperature by the water set free in the reaction, the change may be represented (van't Hoff and Kenrick, *Sitzungsber. K. Akad. Wiss. Berlin*, 1897, 508) by the equation:

$$MgCl_2,6H_2O + 1{\cdot}188CaCl_2,6H_2O = \\ 0{\cdot}252CaCl_2,2MgCl_2,12H_2O + 0{\cdot}101(100H_2O,9{\cdot}27CaCl_2,4{\cdot}92MgCl_2).$$

The temperature at which this change takes place under atmospheric pressure can be determined with great precision, and has been given by one of us (Dawson, *Zeitsch. physikal. Chem.*, 1902, **39**, 27) as 22·40°. At this temperature, the solution ($100H_2O,9{\cdot}27CaCl_2,4{\cdot}92MgCl_2$) is in equilibrium with three solid phases: tachhydrite, calcium chloride hexahydrate, and magnesium chloride hexahydrate.

In the experiments recorded here, about 50 grams of crystallised magnesium chloride and 60 grams of crystallised calcium chloride, corresponding approximately with the proportions of the two substances on the left side of the above equation, were heated at a temperature not exceeding 30° until the formation of tachhydrite was complete. The mixture was then allowed to cool slowly in the air until the temperature had fallen to nearly 22°, when the tube containing it was placed in its outer jacket immersed in a thermostat at 19—20°. When the desired amount of supercooling, 0·3° to 0·4°, had been obtained, minute crystals of the two simple chlorides were added to start the reaction represented by the equation in the direction from right to left.

The calcium chloride used had the composition $CaCl_2,6{\cdot}07H_2O$; the magnesium chloride corresponded with the formula $MgCl_2,6{\cdot}11H_2O$. The small amounts of water, in excess of that required for the pure hexahydrates, give rise to the formation of a considerable amount of solution, but this can be calculated from the known composition of the solution. This may be illustrated in reference to the first experiment in table III. The 52·9 grams of $MgCl_2,6{\cdot}11H_2O + 61{\cdot}6$ grams of $CaCl_2,6{\cdot}07H_2O$ correspond with 0·2576 molecule of $MgCl_2,6H_2O + 0{\cdot}2795$ molecule of $CaCl_2,6H_2O + 0{\cdot}0480$ molecule of water. If x and y denote the number of molecules of $MgCl_2,6H_2O$ and $CaCl_2,6H_2O$ dissolved by 0·048 molecule of water, and if z similarly denotes the number of formula weights of the solution

$$(100H_2O,9{\cdot}27CaCl_2,4{\cdot}92MgCl_2)$$

which are thereby formed at the transition temperature, we obtain the equation:

$$x\mathrm{MgCl_2,6H_2O} + y\mathrm{CaCl_2,6H_2O} + 0{\cdot}048\mathrm{H_2O} = z(\mathrm{100H_2O,9{\cdot}27CaCl_2,4{\cdot}92MgCl_2}),$$

from which, by equating corresponding terms, we have:

$$x = 4{\cdot}92z,\ y = 9{\cdot}27z,\ 100z = 6x + 6y + 0{\cdot}048$$

$$\text{or}\quad x = 0{\cdot}0299,\ y = 0{\cdot}0159,\ z = 0{\cdot}00323.$$

The weight of saturated solution which results from the excess of water in the crystallised magnesium and calcium chlorides amounts therefore to $z \times$ formula weight of solution:

$$(\mathrm{100H_2O,9{\cdot}27CaCl_2,4{\cdot}92MgCl_2}) = z \times 3300 = 10{\cdot}66 \text{ grams},$$

which is about one-eighth of the total weight of solution yielded by the formation of tachhydrite. From this, it is evident that a careful estimation of the water content of the substances employed in the experiments is necessary before the weight of the solution in which the foreign substance is dissolved can be ascertained. Table III contains the data for three experiments:

TABLE III.

Weight of magnesium chloride in grams.	Weight of calcium chloride in grams.	Weight of solution in grams.	Weight of carbamide in grams.	Observed lowering of temperature.	Molecular lowering.
52·9	61·6	80·8	0·3812	0·410°	52·4
49·75	61·45	80·4	0·4274	0·430	48·6
49·48	64·45	84·2	0·4562	0·455	50·5
				Mean.........	50·5

When the complex nature of the change involved in the tachhydrite formation is considered, the concordance of the values obtained in the three independent experiments must be considered very satisfactory.

Some further experiments, made to determine the depression of the temperature at which sodium carbonate decahydrate is transformed into a lower hydrate, have not given sufficiently concordant results to justify their inclusion in the present paper, and these experiments are being continued.

The changes in multi-component systems, for which the depression of the characteristic transition temperatures on the addition of small quantities of foreign substances has been quantitatively determined, are summarised in the following table. The equations representing the changes in terms of the various transition solutions, and the values of the molar depressions, referred to 100 grams of these solutions, are given. By means of these constants, determinations of the molecular weights of substances in aqueous solutions may be made at a series of temperatures between 0° and 100°. Between the values of the constants, the heat changes associated with the chemical processes, and the temperatures at which the transitions occur, a similar relationship exists as is well known to hold between molar freezing-point depressions, latent heats of liquefaction, and absolute freezing temperatures in the case of pure liquids.

Chemical change.	Molar depression.
$Na_2SO_4,10H_2O = 0\cdot367Na_2SO_4 + 0\cdot10(100H_2O,6\cdot33Na_2SO_4)$	28·5
$MgCl_2,6H_2O = 0\cdot0795MgCl_2,4H_2O + 0\cdot0568(100H_2O,16\cdot2MgCl_2)$	76
$(Rb_2C_4H_4O_6)_2,4H_2O = 0\cdot73d\text{-}Rb_2C_4H_4O_6 + 0\cdot73l\text{-}Rb_2C_4H_4O_6 + 0\cdot04(100H_2O,13\cdot48Rb_2C_4H_4O_6)$	37
$Na_2S_2O_3,5H_2O = 0\cdot14Na_2S_2O_3,2H_2O + 0\cdot0472(100H_2O,18\cdot20Na_2S_2O_3)$	43
$NaBr,2H_2O = 0\cdot589NaBr + 0\cdot02(100H_2O,20\cdot54NaBr)$	34·5
$MgCl_2,6H_2O + 1\cdot188CaCl_2,6H_2O = 0\cdot252CaCl_2,2MgCl_2,12H_2O + 0\cdot101(100H_2O,9\cdot27CaCl_2,4\cdot92MgCl_2)$	50·5

ADDENDUM.

Since the above experiments were completed, two papers have appeared bearing the title "Molten Hydrated Salts as Solvents for the Freezing-Point Method." In the first (*J. Amer. Chem. Soc.*, 1907, **29**, 1168), J. L. R. Morgan and H. K. Benson have examined the influence of foreign substances on the freezing points of $CaCl_2,6H_2O$, $LiNO_3,3H_2O$, and $Na_2CrO_4,10H_2O$, and in the second (*ibid.*, p. 1439), Morgan and F. T. Owen have determined the molar freezing-point depressions of $Ca(NO_3)_2,4H_2O$, $Zn(NO_3)_2,3H_2O$, and of $Mn(NO_3)_2,3H_2O$. The invariant points involved in these cases appear to be true freezing points, although in the case of sodium chromate it is not quite clear whether the temperature investigated is the melting point of the decahydrate or the temperature at which this is converted into the hexahydrate. The authors, however, appear to regard their work as a continuation of that of Löwenherz (*loc. cit.*) on sodium sulphate, but this is not the case, for the change which $Na_2SO_4,10H_2O$ undergoes at 32·4° is accompanied by the appearance of a new solid phase.

PHYSICAL CHEMISTRY LABORATORY,
THE UNIVERSITY, LEEDS.

XXXIV.—*Malacone, a Silicate of Zirconium.*

By ALEXANDER CHARLES CUMMING, D.Sc.

A RECENT paper by Kitchin and Winterson (Trans., 1906, **89**, 1568) has directed attention to malacone, and to the fact that it is the only mineral known to contain argon. It is radioactive, and these authors were the first to find uranium in it, although Strutt (*Proc. Roy. Soc.*, 1904, **73**, *A*, 191) had previously suggested that this metal was present.

The identity of the zirconium was proved by Kitchin and Winterson, who prepared from the mineral a pure sample of zirconium oxychloride. The crude zirconium oxychloride gave a ratio of 1 : 1·824 for zirconium to chlorine, as against 1 : 2·01 for a sample of zirconium oxychloride of known purity, and it was only after thirteen recrystallisations from alcohol that they obtained a pure specimen of zirconium oxychloride. The authors found that their crude oxychloride contained some uranium, but the total uranium found in the mineral was insufficient to affect appreciably the purity of the zirconium oxychloride.

When the mineral had been separated into its constituents, Kitchin and Winterson found that the radioactivity emanated from the zirconia. This was a surprising observation, as the zirconia had been boiled with hydrochloric acid, which should have extracted any ordinary radioactive material, and zirconium salts are not themselves radioactive. It seemed, therefore, desirous that these facts should be further investigated.

EXPERIMENTAL.

A complete analysis of the mineral was not thought necessary, but, in the course of certain separations, values for the silica and zirconia were obtained which differed considerably from those given by Kitchin and Winterson. The results obtained, together with those of previous investigators, are given in the following table:

Locality of specimen.	Authority.	SiO_2.	ZrO_2.	$SiO_2 + ZrO_2$.
1 Hitterö	Scheerer[1]	31·31	63·4	94·7
2 Ilmengebirge ...	Hermann[2]	31·87	59·8	91·7
3 Chanteloupe ...	Damour[3]	30·87	61·17	92·0
4 Chanteloupe ...	Rammelsberg[4]	31·05	61·44	92·5
5	Kitchin and Winterson[5]	22·53	67·8	90·3
6	Cumming	32·3	60·5	92·8

[1] Scheerer (*Pogg. Ann.*, 1844, **62**, 436).

[2] Hermann (*J. pr. Chem.*, 1851, **53**, 32).

[3] Damour (*Ann. Chim. Phys.*, 1848, **24**, 87).

[4] Rammelsberg (*Mineralchemie*, p. 891).

[5] *Loc. cit.* The specimens examined by Kitchin and Winterson and by myself were obtained from the Christiania Mine Kompani.

The results obtained thus agreed well with those of early investigators and with the formula (ZrO_2,SiO_2) for the silicate, but differed widely from those of Kitchin and Winterson. The explanation probably lies in the unusual stability of zirconium silicate towards hydrofluoric acid. Repeated evaporations, usually about ten, are necessary to drive off all the silica. There is a possible source of error in this process, as it was found that zirconium was also readily expelled unless a large amount of sulphuric acid was present. After treatment, the zirconium is left mainly as zirconium sulphate, and, if the quantity exceeds 0·5 gram, prolonged ignition is necessary to ensure complete reduction to oxide.

Identity of the Zirconium.—The change of sulphate to oxide on ignition was adopted as a test of the identity of the zirconium salts obtained from malacone. It was carried out as follows: a small unweighed sample of the oxychloride was placed in a platinum crucible, concentrated sulphuric acid added, the mixture evaporated gently to dryness, and weighed as sulphate. More sulphuric acid was then added, and again evaporated. The weight was usually unchanged. The residue was then strongly ignited until of constant weight, and weighed as oxide.

The results of some of the blank experiments were as follows:

Salt used.	Weight as sulphate.	Weight as oxide.	Oxide in sulphate, per cent.
Zirconium nitrate	1·0607	0·4518	42·6
Zirconium oxychloride.	0·3054	0·1315	43·2
	0·3804	0·1718	45·2
Uranium acetate	0·2118	0·1552	73·6

The theoretical percentage of oxide in pure zirconium sulphate is 43·4. It was found that values between 43·2 and 43·5 could always be obtained by starting from pure zirconium oxychloride. Expt. 3 is the result with a specimen to which a little uranium acetate had been added; it was further distinguished from a pure zirconium salt, as the oxide obtained was green, whilst pure zirconia is white. The results for pure uranium acetate agree with the probable change, that is, from uranyl sulphate, UO_2SO_4, to uranyl oxide, U_3O_8, the theoretical percentage of oxide being 74·8.

The oxide to sulphate ratio was thus proved to be a good test of the purity of a zirconium salt, particularly as regards uranium.

Partial Separation into Constituents.—After removal of the silica, a very convenient separation was effected by boiling for about one hour with concentrated hydrochloric acid containing a little nitric acid. The residue was found to be almost pure zirconia, and very little of the zirconia had dissolved. These two portions were examined separately, and are referred to later as the acid-soluble portion and part insoluble in acid respectively.

Part Insoluble in Acid.—9·986 Grams of this part were treated with hydrofluoric acid to remove most of the silica. After ignition, the weight was 7·22 grams. This was made into balls with wood charcoal and sugar, and the mixture heated in a covered crucible. The coke-like mixture was then ignited in a stream of chlorine saturated with carbon tetrachloride at about 60°.

A white, crystalline chloride was collected, which proved to be zirconium tetrachloride. This was washed with water, with which it reacted vigorously, and yielded on evaporation 7·2 grams of oxychloride.

The residue in the tube weighed 3·1 grams, part of which was the ash from the 15 grams of charcoal used.

The oxychloride was found to give all the ordinary tests for zirconium. A trace of iron was present, but no uranium could be detected. The equivalent was determined with the following result:

0·1664 gram of oxychloride gave 0·1920 gram of sulphate.

Weight as oxide = 0·0836 gram.

Oxide in sulphate = 43·6.

The theoretical value for zirconium is 43·4 per cent.

On account of the ash, it was useless to proceed further with this experiment. An attempt was next made to test the homogeneity of the part of malacone insoluble in acid by fractional chlorination.

For this purpose, 20 grams of the part insoluble in acid were evaporated once with hydrofluoric and sulphuric acids to remove the bulk of the silica. After ignition, the residue weighed 15·51 grams. This was mixed with sugar-carbon and chlorinated, but after five hours' chlorination the chloride obtained yielded only 0·62 gram of oxychloride (fraction *A*).

The sugar-carbon was burnt off, as it was evidently unsuitable, and wood charcoal, which had been boiled for some hours in concentrated hydrochloric acid, substituted.

The second chlorination yielded 4·52 grams of oxychloride (fraction *B*). The third chlorination yielded 7·95 grams of oxychloride (fraction *C*), and the fourth chlorination yielded 2·9 grams of oxychloride (fraction *D*). The carbon and silica were removed from the residue, which then weighed 2·1 grams (fraction *E*).

Fraction.	Total weight.	Weight of sample		Percentage oxide in sulphate.
		as sulphate.	as oxide.	
A	0·62	0·5196	0·2238	43·2
B	4·52	0·2047	0·0875	42·8
C	7·95	0·1302	0·0565	43·4
D	2·90	0·5025	0·2200	43·7

For zirconium, the amount of oxide in sulphate is 43·4 per cent. Each fraction gave all the zirconium tests, and in all cases the oxide obtained was pure white; a trace of iron was noticed in each case, and with fraction *A* a yellow colour was obtained with hydrogen peroxide, which probably indicated the presence of titanium in this fraction. In no case could uranium be detected, although it was carefully tested for, and could be readily recognised if a trace were afterwards added. Fraction *E*, the residue from the chlorinations, was qualitatively examined and found to contain zirconia, a ferric salt, and a calcium salt, the latter being probably derived from the charcoal.

Radioactivity.—The part of malacone which did not dissolve in hydrochloric acid, that is, the zirconia and silica, was found to be non-radioactive. This was ascertained by placing 20 grams in a flask with some dilute hydrochloric acid and exhausting the flask. At the end of a week, some air was admitted and then pumped off in the usual manner, but no evidence of radioactivity was found. As a further test, 19 grams of the crude oxychloride collected in the various chlorinations were kept in an exhausted flask for seven days, and the flask washed out thoroughly with successive small quantities of air. The oxychloride proved so completely free from any radioactive material that this air did not affect the leak of an electroscope which had a period of eight hours per twenty divisions.

At first sight, this is in direct opposition to the experience of Kitchin and Winterson, who found that all the radioactive matter remained with the zirconia, but the explanation is probably to be found in the different previous treatment. In their case, the malacone had been fused with fusion mixture, and they mention that it was necessary to use ten times as much fusion mixture as mineral. It is very possible that this contained sufficient sulphate to transform any traces of barium, calcium, or strontium into sulphates, and these would carry down also the radioactive matter as radium sulphate, which would not dissolve in the hydrochloric acid, but would remain with the precipitated zirconia.

Part Soluble in Acid.—This part was found to contain all the radioactive matter. The emanation from the portion of 100 grams of malacone soluble in acid was collected and introduced into an electroscope in the usual manner.

Several measurements were made of the time taken for the activity to fall from its maximum to one-half, and the results varied between 3·5 and four days. In all cases, the activity had almost reached the maximum value two hours after introduction into the electroscope, and after three hours began to fall.

There seems, therefore, no reason to suspect the presence of any radioactive element other than radium, so that the presence of argon cannot be explained on this ground.

Summary.

The formula ZrO_2,SiO_2 corresponds more closely with the observed composition of malacone than does the formula $3ZrO_2,2SiO_2$ which has been recently assigned to it. A detailed examination gave no

reason for doubting the identity of the zirconia, or to suspect the presence of an unknown impurity. The radioactivity can be sufficiently explained by the presence of radium.

This investigation was undertaken at the suggestion of Sir William Ramsay, to whom my best thanks are due. I desire also to thank Dr. A. McKenzie for facilities to continue the work at Birkbeck College.

UNIVERSITY COLLEGE, } LONDON.
BIRKBECK COLLEGE, }

XXXV.—*The Influence of Solvents on the Rotation of Optically Active Compounds. Part XI. Ethyl Tartrate in Aliphatic Halogen Derivatives.*

By THOMAS STEWART PATTERSON and DAVID THOMSON, M.A., B.Sc. (late Carnegie Research Scholar).

IN a former part of this investigation (Trans., 1905, **87**, 313), it has been shown that the influence of chloroform in modifying the rotation of ethyl tartrate is of particular interest, since it was found that the specific rotation of dilute solutions of the ester is unusually low, whilst the corresponding molecular solution-volume has a higher value than in other solvents hitherto examined. Support was thus lent to the suggestion that the rotation of ethyl tartrate in solution varies inversely with molecular solution-volume, and it seemed of some importance to ascertain whether in other halogen-containing solvents, especially perhaps in those of density greater than chloroform, this regularity might be traced still further.

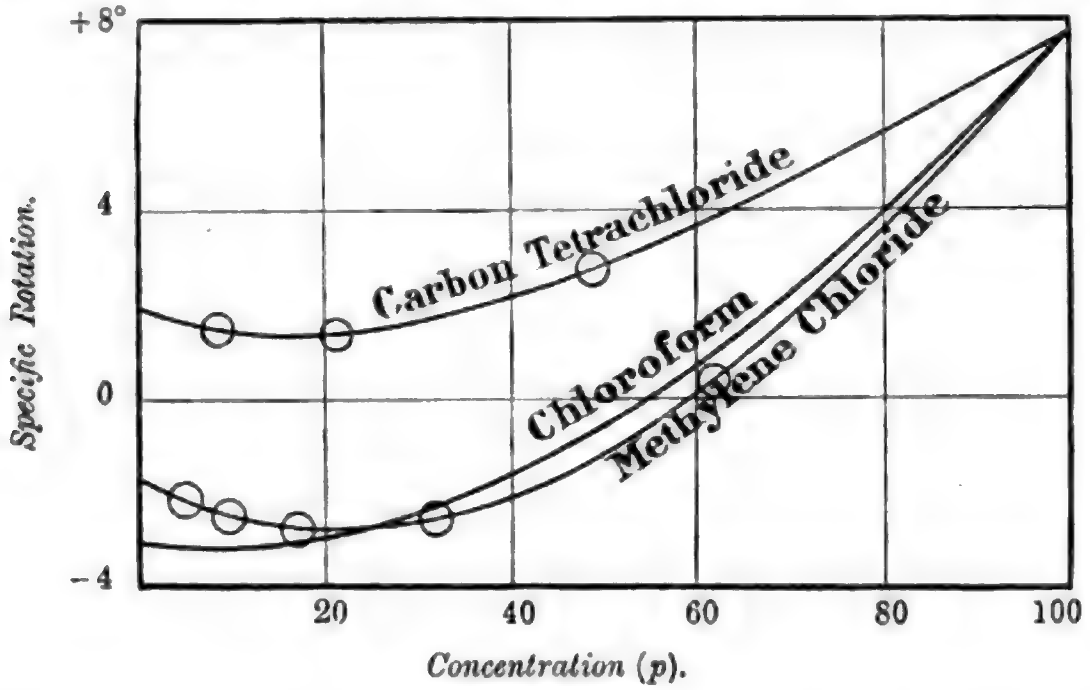
The following pages give an account of work carried out with this object. The solvents used were methylene chloride, carbon tetrachloride, ethylene chloride, ethylidene chloride (*as*-dichloroethane), acetylene tetrachloride (*s*-tetrachloroethane), bromoform, ethyl bromide, ethylene bromide, acetylene tetrabromide (*s*-tetrabromoethane), methyl iodide, methylene iodide, and ethyl iodide. Three or four solutions of ethyl tartrate in each of these solvents were prepared and their rotations determined at several temperatures. From the data obtained, the specific rotations at 20° have been arrived at by interpolation, whilst from the density observations the corresponding molecular solution-volumes have been obtained.

We had hoped that these two variables would be found to show the same relationship as in other cases, but in this we were, in large measure, disappointed, although the relationship does hold to some extent. Thus in all the solvents under consideration the rotation of the dissolved ethyl tartrate is depressed below that of the homogeneous ester, whilst, on the other hand, the molecular solution-volume becomes greater than the molecular volume. Amongst the individual data, also, an inverse proportionality often obtains, but a correlation between the two variables cannot be traced through all the solvents examined, since exceptions are both numerous and important.

It is unnecessary to discuss our results in any great detail; the chief points of interest can best be seen from the four accompanying diagrams, which summarise the research, and in which specific rotation is plotted relative to concentration. The molecular solution-volume curves are not given, as they are all of one type and can be just as well represented by numbers as by graphs.*

Fig. 1.

Ethyl Tartrate in Methylene Chloride, Chloroform, and Carbon Tetrachloride at 20°.



In Fig. 1 are shown the concentration-rotation curves for methylene chloride, chloroform,† and carbon tetrachloride. The curves are of a similar character, but lie perhaps scarcely in the order that might have been expected. At a concentration of $p=30$, the lowest (greatest negative) rotation is found in methylene chloride and the highest in carbon tetrachloride, but at great dilution the rotation in methylene chloride lies between the values in the other two solvents. This is due to the occurrence in each case of a concentration of minimum rotation, which in chloroform is scarcely perceptible, in carbon tetrachloride is clearer ($p=20$; $[\alpha]_D^{20°}$ +1·35°), and in methylene chloride is still more distinct ($p=20$; $[\alpha]_D^{20°}$ −2·83°).

---

* The experimental data are collected together at the end of the paper. The interpolated values for the density of the pure solvents ($p=0$) at 20°/4° and for $[\alpha]_D^{20°}$ of the various solutions are given with the molecular solution-volume data on p. 371.

† See footnote (*) p. 357.

To compare the rotations of these solutions with the molecular solution-volumes, both at infinite dilution, we have the following table:

Solvent.	$[\alpha]_D^{20°}$.	M.S.V.$^{20°}$.
Carbon tetrachloride	+1·9°	173·9 c.c.
Methylene chloride...............	−1·6	174·1 ,,
Chloroform	−3·0*	177·5 ,, †

These numbers stand in inverse order, the lowest rotation corresponding with the greatest solution-volume, and they therefore exhibit the relationship we had expected to find, but it must be admitted that the very small difference between the molecular solution-volume in methylene chloride and carbon tetrachloride seems scarcely sufficient to account for the considerable difference in rotation.

In Fig 2 are shown curves for the other chlorides examined. It will be observed that those for ethylidene chloride and methylene chloride (Fig. 1) are very similar, so that the substitution of one of the hydrogen atoms in the latter compound by a methyl group causes very little change in the solvent influence of the resulting ethylidene chloride. A minimum rotation is somewhat more pronounced in ethylidene chloride ($p=25$; $[\alpha]_D^{20°}$ −3°), but the value of the rotation at infinite dilution is very nearly the same in both.

On the other hand, a distinct difference is noticeable between the solvent influences of ethylene chloride and ethylidene chloride. From $p=100$ to $p=35$, the two curves lie very close together, but at less concentrations they diverge. The rotation in ethylene chloride continues to diminish, and no concentration of minimum rotation is apparent.

The introduction of two chlorine atoms into the molecule of ethylene chloride to form acetylene tetrachloride is attended by a very considerable change in solvent influence. In the latter solvent, the rotation of the dissolved ethyl tartrate diminishes very rapidly with

---

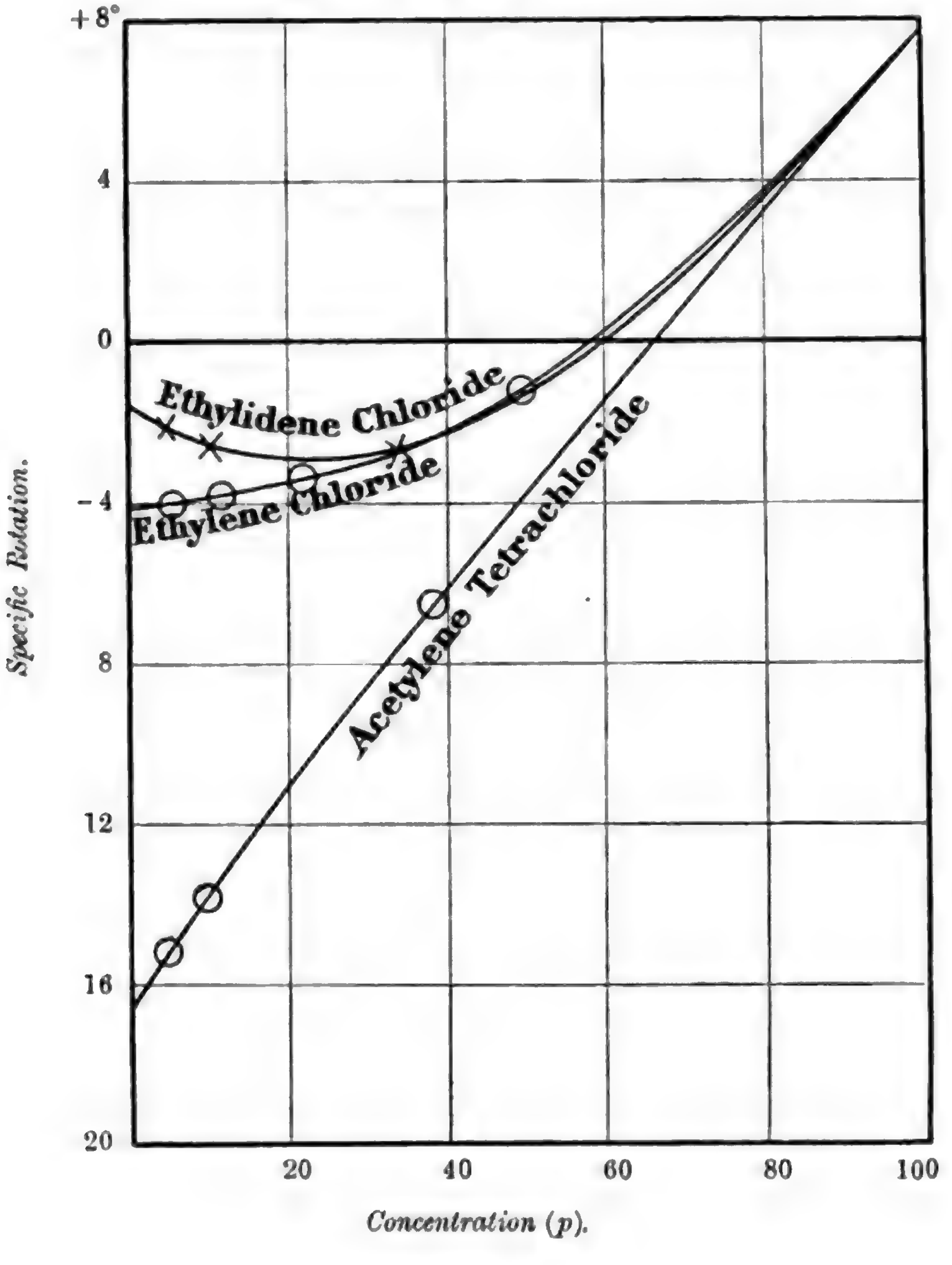
[*] Reproduced from Trans., 1905, **87**, 313, where the rotation at infinite dilution was taken as −3·2°, the slightly higher value in a solution of $p=2$ ($[\alpha]_D^{20°}$ −3·1°) as compared with that for a solution of $p=8·99$ ($[\alpha]_D^{20°}$ −3·15°) being attributed to experimental error. On account of the behaviour of carbon tetrachloride and methylene chloride, however, it is probable that a concentration of minimum rotation exists in chloroform solution, and that the rotation at infinite solution is −3·0° instead of −3·2° as formerly assumed.

[†] We are of opinion that this value is rather too high.

diminishing concentration, attaining ultimately to a value of $-16{\cdot}6°$, inactivity being already reached in a solution of $p = 66{\cdot}5$. The total depression of rotation (from $+7{\cdot}76°$ to $-16{\cdot}6°$) is thus more than twice as great as in ethylene chloride. It is noticeable, also, that this curve is concave with reference to the lower right-hand corner of the diagram. The other curves are convex.

FIG. 2.

Ethyl Tartrate in Ethylidene Chloride, Ethylene Chloride, and Acetylene Tetrachloride at 20°.



The values for the molecular solution-volume of ethyl tartrate in these solvents are of considerable interest, since in acetylene tetrachloride, where the rotation is so unusually low, the volume should be correspondingly great:

Solvent.	$[\alpha]_D^{20^\circ}$ (infinite dilution).	M.S.V.$^{20^\circ}$ (infinite dilution).
Ethylidene chloride	$-1{\cdot}7^\circ$	172·8 c.c.
Ethylene chloride	$-4{\cdot}2$	176·0 ,,
Acetylene tetrachloride	$-16{\cdot}6$	173·4 ,,

It will be seen from the table that the inverse proportionality between the two variables does occur in the first two solvents. The rotation is lower and the solution-volume greater in ethylene chloride than in ethylidene chloride, but it is not possible to reconcile the data for acetylene tetrachloride with those for the other two solvents; the solution-volume does not show an increase by any means corresponding with the very low value of the rotation.

Curves representing the behaviour of the solvents containing bromine are shown in Fig. 3. The specific rotation of the ethyl bromide solutions diminishes fairly rapidly with increasing dilution, so as to become zero at $p=38$. In solutions less concentrated than this, the rotation varies more slowly, and after $p=10$ there is practically no change. A concentration of minimum rotation perhaps occurs, but if so, it is by no means distinct.

In bromoform, the rotation varies less with dilution than in ethyl bromide, never falling below zero. In addition, the curve is concave, and thus presents a distinct contrast to the curves for ethyl bromide and the chlorides. Bromoform, it may also be noticed, has a much less pronounced effect than chloroform.

From Figs. 1 and 2, it will be seen that ethylene chloride is similar to chloroform in its solvent influence, but somewhat more powerful. In an analogous manner, ethylene bromide* gives a curve of the same type as bromoform, concave, and at the same time is vastly more powerful. The influence of ethylene bromide becomes greater as the dilution increases, so that as the concentration changes from $p=10$ to $p=0$ the rotation falls from -10° to $-18{\cdot}8^\circ$, or one-third of the total change.

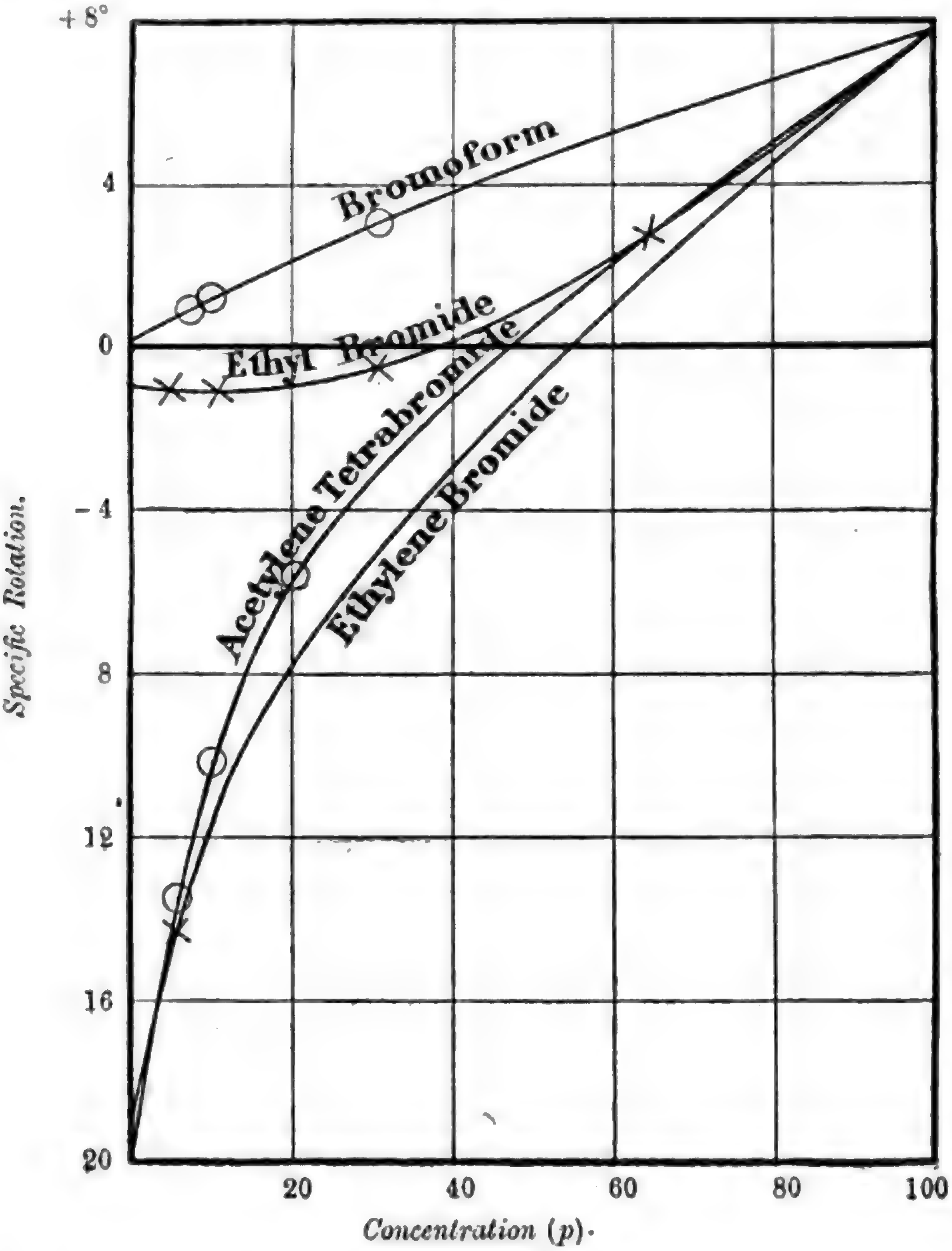
The introduction of two more bromine atoms into the molecule to form acetylene tetrabromide is not attended by any very marked alteration in solvent influence, and is thus in distinct contrast to the behaviour observed in the case of the corresponding chlorides, acetylene tetrachloride having, as has been pointed out, a very much greater effect than ethylene chloride. The curve for acetylene tetrabromide is concave like those for bromoform and ethylene bromide; for more concentrated solutions, the influence of acetylene tetrabromide is somewhat less than that of ethylene bromide, but in very dilute solution the effects produced by these two solvents are practically the same.

---

* The data from which the curve is plotted are those given by Winther, "*Bidrag til den optiske drejnings Teori,*" København, 1907, p. 34; *Zeitsch. physikal. Chem.*, 1907, **60**, 578. The one solution examined by us is represented by a cross in the diagram. Our value, $-14{\cdot}3^\circ$, for a solution of $p=5{\cdot}59$ agrees well with Winther's value of $-14{\cdot}16^\circ$ for a solution of $p=5{\cdot}53$.

FIG. 3.

Ethyl Tartrate in Bromoform, Ethyl Bromide, Ethylene Bromide, and Acetylene Tetrabromide at 20°.



In the table below are given data for solution-volume and rotation in these bromides:

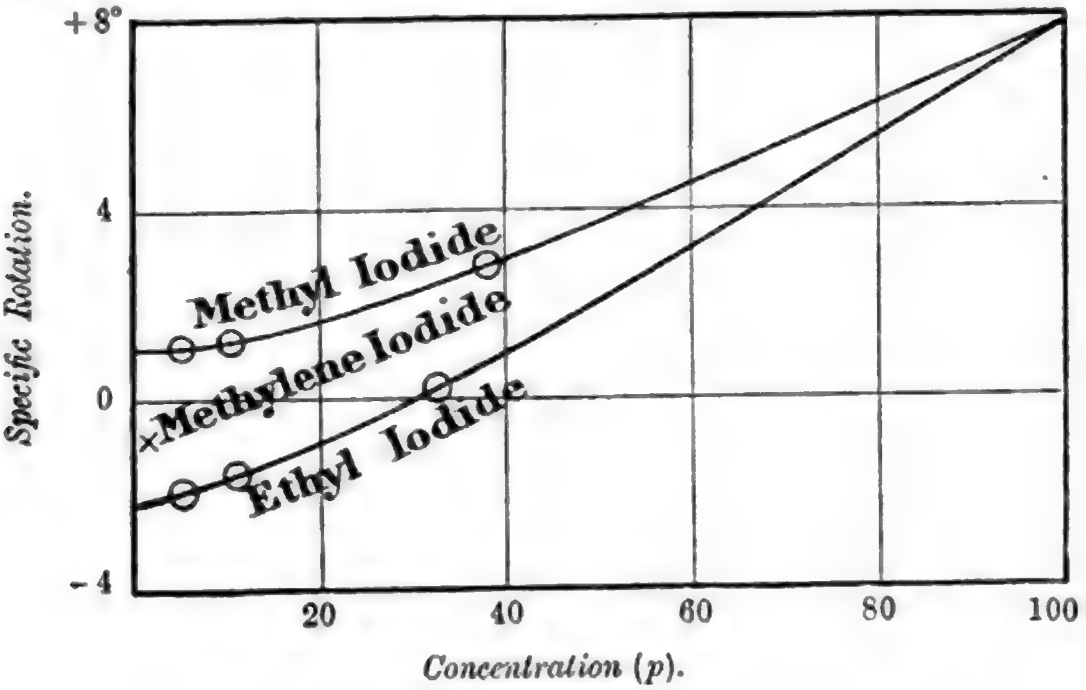
Solvent.	$[\alpha]_D^{20°}$ (infinite dilution).	M.S.V.$^{20°}$ (infinite dilution).
Bromoform	+0·2°	177·0 c.c.
Ethyl bromide	-0·95	172·6 ,,
Ethylene bromide	-18·8	176·7 ,, ($p=5·6$)
Acetylene tetrabromide	-20·0	176·8 ,,

Acetylene tetrabromide and ethylene bromide, in which the rotations are very low and almost equal, give solution-volumes which are high and almost equal, whilst in ethyl bromide a much higher rotation is accompanied by a considerably smaller solution-volume, but it is obvious that the data for bromoform are entirely out of harmony with the others; the rotation is higher than in ethyl bromide, whilst the volume is even greater than in acetylene tetrabromide.

In Fig. 4 are shown curves for the iodides examined. Methyl iodide affects the rotation of ethyl tartrate in somewhat the same manner and to much the same extent as does carbon tetrachloride. The curve is of the convex type, like those for the chlorides; it does not cut the zero axis, and there seems to be no concentration of minimum rotation.

FIG. 4.

Ethyl Tartrate in Methyl Iodide, Methylene Iodide, and Ethyl Iodide at 20°.



The curve for ethyl iodide is similar to that for methyl iodide, but lies wholly below it. The substitution of one of the hydrogen atoms in methyl iodide by a methyl group causes therefore a greater depressing influence in the resulting, as compared with the original, substance. A similar, but less decided, effect was noticed in comparing methylene chloride and ethylidene chloride. It might perhaps have been expected that the greater the proportion of halogen in the solvent the greater would be the effect produced, but this is not the case, as is shown by the above instances as well as by several others recorded in this paper.

We also attempted to use methylene iodide as a solvent, but were surprised to find that ethyl tartrate is only very slightly soluble in it, so that we were unable to examine more than one mixture, the specific rotation of which (– 0·8) lay between those for methyl iodide and ethyl iodide.

Below are given the molecular solution-volume data for these solvents. They relate to concentration $p = 1·4$, since the only solution in methylene iodide was of this strength:

Solvent.	$[\alpha]_D^{20°}$ ($p = 1·4$).	M.S.V.$^{20°}$ ($p = 1·4$).
Methyl iodide	+1·1°	179·0 c.c.
Methylene iodide	– 0·8	177·7 ,,
Ethyl iodide.........................	– 2·18	177·8 ,,

The solution-volume in these three iodides is high; in methyl iodide greater than in any other solvent previously examined. The values of the rotation, however, are not by any means in agreement with this, being in all three cases, in spite of the great density of the solvents, comparatively little depressed and standing, further, in the opposite relationship to solution-volume from what was to be expected. In methyl iodide, where the solution-volume is greater, the rotation is also greater than in ethyl iodide, whilst for methylene iodide and ethyl iodide, in which the volume is almost the same, the rotation is distinctly different.

The method which we have adopted here, that, namely, of dealing with the solvents in classes, is probably the most favourable that could be chosen for exhibiting any presumed relationship, and yet even in these circumstances exceptions to the suggestion that specific rotation varies inversely with solution-volume are numerous and striking, and we do not wish to minimise them. When the solvents are considered indiscriminately, the exceptions become, of course, more obvious, as will be seen from the following table, in which all

Solvent.	$[\alpha]_D^{20}$ of ethyl tartrate (infinite dilution).	M.S.V.^{20} of ethyl tartrate (infinite dilution) in c.c.	N.*	Diel. const.‡	Heat of disgregation.§
Carbon tetrachloride	+1·9°	173·9	13·3	2·2	41·8
Methyl iodide..................	+1·08	179·8	—	7·1	41·7
Bromoform	+0·2	177·1	—	4·4	—
Methylene iodide ($p = 1·4$)..	– 0·8	177·7	—	5·5	—
Ethyl bromide	– 0·95	172·6	20·7†	(9·7 ; 8·9)	54·7
Ethylidene chloride	– 1·7	172·7	20·8	10·8	60·4
Methylene chloride	– 1·6	174·1	26·87†	—	67·9
Ethyl iodide	– 2·2	178·3	14·8†	7·4	42·5
Chloroform	– 3·0	177·5	18·6	5·0	52·9
Ethylene chloride	– 4·2	176·0	24·6	10·9	73·7
Acetylene tetrachloride......	– 16·6	173·6	10·88†	—	—
Acetylene tetrabromide......	– 20·0	176·8	—	—	—
Ethylene bromide	– 18·8	176·8	19·6†	4·9	39·3

* Schiff, *Annalen*, 1888, **223**, 72. † Calculated according to Schiff's formula.

‡ Landolt, Börnstein, and Meyerhoffer, *Tabellen*, p. 769.

§ Calculated from values of heat of vaporisation given in Landolt, Börnstein, and Meyerhoffer, *Tabellen*, p. 505. See Trans., 1901, **79**, 195; 1902, **81**, 1107.

the data referred to are brought together. The solvents are arranged in order of magnitude of the rotation, and, since in former papers a certain connexion seemed traceable between rotation and surface tension, dielectric constant, and heat of disgregation, we have added values found by various observers for these three properties of the solvents used.

It will be seen that there is certainly no greater apparent relationship between the numbers in the last three columns and the values of the rotation than exists between the latter and the data for solution-volume.

Other suggestions which have been made to account for variation of rotation in solution are even less successful. It has been shown already (Trans., 1902, **81**, 1113) that osmotic molecular weight in dilute solution seems to have no connexion with rotation, and a further illustration of this is to be found in the case of ethyl tartrate in ethylene bromide. As Winther (*Bidrag til den optiske drejnings Teori*, p. 42; *Zeitsch. physikal. Chem.*, 1907, **60**, 584) has found, the cryoscopic molecular weight in very dilute solution is normal. Thus in water, benzene, and ethylene bromide, to take only three examples, the molecular weight of ethyl tartrate is normal, whilst the respective specific rotations are +26·96° (Trans., 1904, **85**, 1130), +6·1° (Trans., 1902, **81**, 1107), and −18·8°.

Reference has been made in the previous part of this investigation (Trans., 1907, **91**, 1843) to the possibility of combination of solute and solvent. It is clear, so far as our solutions are concerned, that, since we have at present no means of determining the number of molecules of solvent that combine with one molecule of solute—if such combination occurs at all—and, further, no means of determining the value of the equilibrium constant, an attempt to apply this idea would be premature. Certainly no indications of combination similar to those observed by Irvine (Trans., 1906, **89**, 1568) or by Gennari (*Zeitsch. physikal. Chem.*, 1896, **19**, 130. See also Winther, *Bidrag til den optiske drejnings Teori*, p. 115; *Zeitsch. physikal. Chem.*, 1907, **60**, 681) have been met with by us in the course of these experiments.

EXPERIMENTAL.

The ethyl tartrate used had $\alpha_D^{18\cdot1^\circ}$ +9·153°. The various solvents (which were obtained from Kahlbaum) were purified by washing with dilute alkali and with water, drying with calcium chloride, and distillation, either at atmospheric pressure with a Young column or under reduced pressure.

Ethyl Tartrate in Methylene Chloride.

The boiling point of the methylene chloride was not very steady. The fraction used distilled between 40·25° and 41·75° at atmospheric pressure:

I. $p = 5·11606$.

$t°$	14·7°	20·7°	24·1°	27·0°	30·1°
$\alpha_D^{t°}$ (160 mm.)	−0·308	−0·204	−0·170	−0·116	−0·072
$[\alpha]_D^{t°}$	−2·81	−1·88	−1·57	−1·08	−0·67

II. $p = 9·74502$.

$t°$	16·2°	20·4°	26·5°
$\alpha_D^{t°}$ (160 mm.)	−0·638	−0·480	−0·276
$[\alpha]_D^{t°}$	−3·08	−2·33	−1·35

III. $p = 17·0966$.

$t°$	16·5°	21·3°	25·1°	29·1°
$\alpha_D^{t°}$ (160 mm.)	−1·203	−0·929	−0·733	−0·497
$[\alpha]_D^{t°}$	−3·35	−2·60	−2·06	−1·40

IV. $p = 32·8988$.

$t°$	16·7°	21·6°	25·5°
$\alpha_D^{t°}$ (160 mm.)	−2·050	−1·538	−1·090
$[\alpha]_D^{t°}$	−3·02	−2·27	−1·62

V. $p = 61·88$.

$t°$	19·0°	26·9°	30·9°	32·3°	34·7°
$\alpha_D^{t°}$ (160 mm.)	+0·280	+1·818	+2·588	+2·862	+3·320
$[\alpha]_D^{t°}$	+0·23	+1·48	+2·12	+2·35	+2·73

Densities determined:

Solvent.		I.		II.	
$t°$.	d.	$t°$.	d.	$t°$.	d.
18·05°	1·3397	19·34°	1·32865	18·57°	1·32249
20·77	1·33467	22·85	1·32246	21·25	1·31792
26·23	1·32464	25·96	1·31693	28·13	1·30607

III.		IV.		V.	
$t°$.	d.	$t°$.	d.	$t°$.	d.
20·37°	1·30830	19·5°	1·28704	18·86°	1·24867
22·11	1·30563	22·88	1·28207	21·42	1·24549
27·20	1·29719	27·33	1·27536	26·45	1·23926

Ethyl Tartrate in Carbon Tetrachloride.

The carbon tetrachloride boiled very steadily at 75·75—75·84°:

I. $p = 8·82387$.

$t°$	18·6°	19·5°	20·9°	25·2°	27·9°	30·2°
$\alpha_D^{t°}$ (160 mm.)	0·266	0·324	0·368	0·54	0·612	0·694
$[\alpha]_D^{t°}$	1·21	1·48	1·68	2·49	2·83	3·22

II. $p = 21·224$.

$t°$	16·7°	26·8°	31·5°	35·8°
$\alpha_D^{t°}$ (160 mm.)	0·467	1·191	1·509	1·855
$[\alpha]_D^{t°}$	0·92	2·37	3·02	3·73

III. $p = 48·926$.

$t°$	16·9°	22·3°	26·5°	30·9°	35·3°	39·4°
$\alpha_D^{t°}$ (100 mm.)	1·596	2·014	2·524	2·894	3·170	3·598
$[\alpha]_D^{t°}$	2·36	3·00	3·77	4·35	4·78	5·45

Densities determined :

Solvent.		I.		II.		III.	
t°.	*d.*	*t°.*	*d.*	*t°.*	*d.*	*t°.*	*d.*
19·35°	1·59555	18·91°	1·55059	18·1°	1·49349	20·08°	1·37606
21·8	1·59114	23·07	1·54292	23·44	1·48459	23·38	1·37155
30·4	1·5742	29·60	1·53091	27·56	1·47761	25·64	1·36817
58·2	1·5196	—	—	29·54	1·47421	32·76	1·35838

Ethyl Tartrate in Ethylene Chloride.

The ethylene chloride used boiled very steadily at 82·97—83° under atmospheric pressure :

I. $p = 5·8702$.

$t°$	15·9°	19·0°	39·8°	45·5°
α_D^t (160 mm.)	−0·548	−0·492	−0·202	−0·128
$[\alpha]_D^t$	−4·65	−4·19	−1·76	−1·12

II. $p = 11·733$.

$t°$	13·9°	18·4°	36·9°	41·5°
α_D^t (160 mm.)	−1·085	−0·943	−0·341	−0·171
$[\alpha]_D^t$	−4·61	−4·03	−1·48	−0·75

III. $p = 22·0379$.

$t°$	13·6°	16·8°	20·6°	24·2°	26·0°	29·6°
α_D^t (100 mm.)	−1·249	−1·115	−0·891	−0·721	−0·607	−0·439
$[\alpha]_D^t$	−4·54	−4·07	−3·27	−2·65	−2·24	−1·62

IV. $p = 49·7182$.

$t°$	14·7°	18·2°	23·3°	27·2°	30·9°
α_D^t (100 mm.)	−1·298	−0·906	−0·484	+0·02	+0·386
$[\alpha]_D^t$	−2·12	−1·48	−0·79	+0·03	+0·64

Densities determined :

Solvent.		I.		II.	
t°.	*d.*	*t°.*	*d.*	*t°.*	*d.*
18·5°	1·25569	18·66°	1·25058	18·76°	1·24630
21·42	1·25141	20·27	1·24829	20·96	1·24322
27·15	1·24303	24·05	1·24287	31·72	1·22819

III.		IV.	
t°.	*d.*	*t°.*	*d.*
18·15°	1·24076	18·15°	1·22641
20·92	1·23711	21·65	1·22217
30·65	1·22404	27·12	1·21553

Ethyl Tartrate in Ethylidene Chloride.

The ethylidene chloride boiled very steadily at 57·4—57·5° :

I. $p = 4·64846$.

t° ……………….	11·5°	16·1°	19·6°	22·8°	25·3°	27·8°
$\alpha_D^{t^\circ}$ (160 mm.) …	−0·345	−0·269	−0·195	−0·129	−0·091	+0·057
$[\alpha]_D^{t^\circ}$ ……………	−3·9	−3·06	−2·23	−1·48	−1·05	+0·66

II. $p = 10·6983$.

t° ………..	11·3°	14·0°	19·6°	21·6°
$\alpha_D^{t^\circ}$(160 mm.)	−0·906	−0·798	−0·544	−0·452
$[\alpha]_D^{t^\circ}$ ……..	−4·44	−3·93	−2·7	−2·25

III. $p = 34·237$.

t°	12·0°	17·0°	24·9°	27·0°
$\alpha_D^{t^\circ}$ (160 mm.)	−2·787	−2·215	−1·067	−0·789
$[\alpha]_D^{t^\circ}$	−4·29	−3·40	−1·65	−1·22

Densities determined :

Solvent.		I.		II.		III.	
t°.	d.	t°.	d.	t°.	d.	t°.	d.
17·6°	1·17922	19·91°	1·17658	19·27°	1·17915	19·9°	1·1855
21·25	1·17354	23·17	1·17157	22·24	1·17471	25·28	1·17822
29·25	1·16097	27·87	1·16445	28·97	1·16467	27·71	1·17504

Ethyl Tartrate in Acetylene Tetrachloride.

The acetylene tetrachloride boiled between 94° and 100° under 15 mm. pressure :

I. $p = 4·96198$.

t° ……………….	15·2°	21·2°	26·9°	31·5°	36·5°
$\alpha_D^{t^\circ}$ (160 mm.)……	−2·075	−1·863	−1·643	−1·453	−1·283
$[\alpha]_D^{t^\circ}$ ……………….	−16·53	−14·93	−13·24	−11·76	−10·44

II. $p = 9·314$.

t° …	16·0°	22·3°	29·1°	33·4°	39·3°	48·2°	66·4°	72·3°	92·8°	101·3
$\alpha_D^{t^\circ}$ (160 mm.)—	−3·436	−3·073	−2·617	−2·349	−1·923	−1·533	−0·705	−0·364	+0·252	+0·556
$[\alpha]_D^{t^\circ}$	−14·81	−13·33	−11·42	−10·30	−8·48	−6·82	−3·19	−1·66	+1·17	+2·61

III. $p = 38·062$.

t° ……………	15·6°	23·1°	27·1°	30·9°	34·6°	37·6°
$\alpha_D^{t^\circ}$ (160 mm.)..	−6·559	−5·085	−4·253	−3·655	−3·113	−2·415
$[\alpha]_D^{t^\circ}$ …………	−7·55	−5·90	−4·94	−4·27	−3·65	−2·84

Densities determined :

Solvent.		I.		II.		IV.	
t°.	d.	t°.	d.	t°.	d.	t°.	d.
18·2°	1·60303	18·79°	1·57512	21·68°	1·54838	17·76°	1·42309
21·1	1·5985	22·23	1·56993	31·92	1·53320	23·41	1·41578
26·62	1·58995	27·44	1·56203	32·50	1·5323	28·27	1·40950
29·27	1·5858	—	—	41·0	1·5198	—	—
—	—	—	—	71·2	1·4747	—	—

Ethyl Tartrate in Bromoform.

The bromoform boiled at 40—47° under a pressure of 10—12 mm. (oil-bath, 80—90°):

I. $p = 7·0809$.

$t°$	16·0°	20·5°	24·8°	39·8°
α_D^{t} (160 mm.)	0·141	0·295	0·447	0·923
$[\alpha]_D^{t}$	0·47	0·99	1·51	3·17

II. $p = 9·9976$.*

$t°$	16·9°	22·6°	38·8°	50·6°	59·1°	76·9°
α_D^{t} (249·6 mm.)	0·540	0·891	1·953	2·633	3·075	3·995
$[\alpha]_D^{t}$	0·86	1·43	3·18	4·34	5·11	6·76

III. $p = 30·915$.

$t°$	14·5°	16·9°	28·9°
α_D^{t} (160 mm.)	2·407	2·741	4·041
$[\alpha]_D^{t}$	2·42	2·76	4·11

Densities determined:

Solvent.		I.		II.*		III.	
t°.	*d.*	*t°.*	*d.*	*t°.*	*d.*	*t°.*	*d.*
19·07°	2·8924	19·04°	2·62003	12·9°	2·5169	19·25°	2·00405
21·17	2·8869	22·56	2·61179	31·0	2·4751	22·67	1·99788
25·75	2·8750	30·03	2·59402	52·0	2·4270	32·17	1·9808
—	—	—	—	73·0	2·3780	—	—

Ethyl Tartrate in Ethyl Bromide.

The ethyl bromide boiled very steadily at 37·8°:

I. $p = 4·9815$.

$t°$	20·1°
α_D^{t} (170 mm.)	−0·119
$[\alpha]_D^{t}$	−0·97

II. $p = 10·92$.

17·1°	21·5°	26·8°
−0·381	−0·240	−0·003
−1·43	−0·91	−0·11

III. $p = 30·576$.

	19·1°	21·5°
(70 mm.)	−0·193	−0·066
	−0·66	−0·22

IV. $p = 65·282$.

$t°$	16·6°	23·5°	24·7°
α_D^{t} (70 mm.)	1·319	1·910	2·003
$[\alpha]_D^{t}$	2·24	3·27	3·43

V. $p = 2·01598$.

Only the density of this solution was examined.

---

* This series of observations was carried out with a different sample of bromoform from that used for the other two series. Unfortunately, by an oversight, its density was not determined, and, therefore, this solution does not appear amongst those for which values of molecular solution-volume are given on p. 371.

Densities determined:

Solvent.		I.		II.	
t°.	*d.*	*t°.*	*d.*	*t°.*	*d.*
18·32°	1·46369	18·7°	1·44652	18·95°	1·42832
19·62	1·46107	19·77	1·44439	22·9	1·42090
22·5	1·45523	20·93	1·44210	27·20	1·41242

III.		IV.		V.	
t°.	*d.*	*t°.*	*d.*	*t°.*	*d.*
18·85°	1·3725	19·57°	1·28320	18·47°	1·4564
19·37	1·37129	20·17	1·28250	19·07	1·4552
20·10	1·39038	21·20	1·28117	21·6	1·4501

Ethyl Tartrate in Ethylene Bromide.

The ethylene bromide boiled very steadily at 34° under a pressure of 14 mm. (oil-bath, 55—58°):

p = 5·58716.

t°	15·4°	18·0°	20·7°	22·7°	42·7°	43·4°
α_D^{t} (160 mm.).	−2·846	−2·762	−2·622	−2·504	−1·734	−1·710
$[\alpha]_D^{t}$	−15·24	−14·82	−14·11	−13·50	−9·53	−9·41

Densities determined:

Solvent.		*p* = 5·58716.	
t°.	*d.*	*t°.*	*d.*
18·1°	2·1856	18·02°	2·08414
21·37	2·17875	20·18	2·07987
30·55	2·15945	27·82	2·06464

Ethyl Tartrate in Acetylene Tetrabromide.

The acetylene tetrabromide boiled steadily at 117° under a pressure of 14 mm. (oil-bath, 155—165°):

I. *p* = 5·6676.

t°	17·7°	20·4°	23·0°	25·4	44·4°
α_D^{t} (160 mm.)	−3·46	−3·324	−3·172	−3·014	−2·028
$[\alpha]_D^{t}$	−13·93	−13·35	−12·85	−12·24	−8·34

II. *p* = 9·9596.

t°	16·2°	19·6°	22·8°	31·7°
α_D^{t} (160 mm.)	−4·53	−4·21	−3·901	−3·146
$[\alpha]_D^{t}$	−11·01	−10·26	−9·54	−7·74

III. $p = 20{\cdot}1106$.

t°	11·7°	12·6°	16·3°	19·8°
$\alpha_{D}^{t^\circ}$ (100 mm.)	−3·244	−3·147	−2·887	−2·505
$[\alpha]_{D}^{t^\circ}$	−7·03	−6·83	−6·28	−5·47

Densities determined :

Solvent.		I.		II.		III.	
t°.	d.	t°.	d.	t°.	d.	t°.	d.
20·87°	2·96182	19·99°	2·72802	19·82°	2·57597	17·76°	2·28204
23·78	2·95518	22·81	2·72193	21·95	2·57167	20·75	2·27661
31·5	2·93797	31·50	2·7038	30·2	2·55516	25·98	2·26694
		45·91	2·6736				

Ethyl Tartrate in Methyl Iodide.

The methyl iodide boiled at 42·12—42·14° under atmospheric pressure:

I. $p = 5{\cdot}19605$.

t°	14·9°	20·3°	28·3°
$\alpha_{D}^{t^\circ}$ (170 mm.)	0·10	0·228	0·410
$[\alpha]_{D}^{t^\circ}$	0·52	1·19	2·16

II. $p = 10{\cdot}4466$.

18·1°	21·5°	24·8°
0·351	0·503	0·653
0·95	1·37	1·78

III. $p = 38{\cdot}0899$.

t°	14·5°	22·2°	24·4°	25·5°
$\alpha_{D}^{t^\circ}$ (100 mm.)	1·327	1·975	2·227	2·311
$[\alpha]_{D}^{t^\circ}$	2·06	3·08	3·48	3·62

Densities determined :

Solvent.		I.		II.		III.	
t°.	d.	t°.	d.	t°.	d.	t°.	d.
18·22°	2·28408	19·39°	2·17168	18·86°	2·07572	18·77°	1·68916
20·85	2·27655	21·03	2·16729	21·02	2·07034	20·89	1·68540
26·35	2·26063	26·62	2·15225	23·16	2·06492	25·12	1·67773

Ethyl Tartrate in Methylene Iodide.

The methylene iodide was washed with dilute alkali, then with water, dried with anhydrous sodium sulphate, and distilled under reduced pressure. It boiled between 66° and 70° under a pressure of 11—12 mm. (oil-bath, 80—90°):

$p = 1{\cdot}4233$.

t°	18·9°	25·7°	32·2°	39·7°	43·6°	46·3°
$\alpha_{D}^{t^\circ}$ (160 mm.)	−0·1	+0·028	+0·108	+0·178	+0·226	+0·234
$[\alpha]_{D}^{t^\circ}$	−1·35	+0·38	+1·47	+2·46	+3·12	+3·24

Densities determined :

Solvent.		$p = 1·4233$.	
t°.	*d*.	*t*°.	*d*.
19·41°	3·32605	21·06°	3·23642
21·5	3·32138	22·91	3·23154
26·75	3·3074	26·72	3·22161
29·15	3·3010	33·48	3·2038

Ethyl Tartrate in Ethyl Iodide.

The ethyl iodide boiled at 72·25—72·3° under atmospheric pressure.

I. $p = 5·17118$.

t°	20·6°	25·2°	27·0°	50·2°
α^{t}_{D} (170 mm.)	−0·3	−0·194	−0·106	+0·462
$[\alpha]^{t}_{D}$	−1·82	−1·19	−0·65	+2·91

II. $p = 10·6333$.

t°	12·8°	19·7°	25·4°	30·6°	45·9°
α^{t}_{D} (170 mm.)	−0·824	−0·465	−0·215	+0·033	+0·519
$[\alpha]^{t}_{D}$	−2·51	−1·42	−0·66	+0·10	+1·63

III. $p = 32·766$.

t°	18·7°	26·2°	29·2	30·6°
α^{t}_{D} (170 mm.)	0·057	1·003	1·389	1·651
$[\alpha]^{t}_{D}$	0·06	1·13	1·57	1·87

Densities determined :

Solvent.		I.		II.		III.	
t°.	*d*.	*t*°.	*d*.	*t*°.	*d*.	*t*°.	*d*.
19·25°	1·93875	18·58°	1·87591	18·22°	1·81533	18·07°	1·60740
20·99	1·93483	19·33	1·87422	20·41	1·81067	20·46	1·60373
24·54	1·92654	21·38	1·86976	21·75	1·80801	25·33	1·59553
32·35	1·90862	24·17	1·86367	26·01	1·79910		
		32·9	1·84426				

Molecular Solution-Volume and Specific Rotation, at 20°, of Ethyl Tartrate in Various Solvents.

Molecular volume of ethyl tartrate at 20° $= \frac{206}{1·2053} = 170·91$ c.c.

For the homogeneous ester, $[\alpha]^{20^\circ}_{D} = +7·76^\circ$.

Solvent.	*p*.	*d* 20°/4°.	M.S.V.$^{20^\circ}$. c.c.	$[\alpha]^{20^\circ}_{D}$.
Methylene chloride	0	1·3361	174·1*	−1·60°*
	5·11606	1·32749	173·73	−2·08
	9·74502	1·32006	173·4	−2·40
	17·0966	1·30890	172·92	−2·79
	32·8988	1·2863	172·32	−2·50
	61·8807	1·2473	171·93	+0·36

* Extrapolated.

Molecular Solution-Volume and Specific Rotation, at 20°, of Ethyl Tartrate in Various Solvents (continued).

Solvent.	p.	d 20°/4°.	M.S.V.$^{20°}$. c.c.	$[\alpha]_D^{20°}$.
Carbon tetrachloride	0	1·59472	173·90*	+1·9*
	8·8239	1·54858	172·79	+1·53
	21·224	1·49033	171·81	+1·38
	48·926	1·3762	171·11	+2·75
Ethylene chloride	0	1·25350	176·0*	−4·20*
	5·8702	1·24868	175·14	−4·07
	11·733	1·24457	174·39	−3·80
	22·0379	1·23833	173·47	−3·40
	49·7182	1·22417	172·26	−1·22
Ethylidene chloride	0	1·17549	172·8*	−1·70*
	4·64846	1·17644	172·2	−2·15
	10·6983	1·17806	171·67	−2·63
	34·237	1·1854	170·97	−2·68
Acetylene tetrachloride...... ...	0	1·60022	173·4*	−16·60*
	4·96198	1·57330	173·1	−15·20
	9·3140	1·5508	172·8	−13·80
	38·0616	1·4202	171·6	−6·55
Bromoform	0	2·8899	177·0*	+0·20*
	7·0809	2·61778	175·93	0·93
	9·9976†	—	—	1·19
	30·915	2·0027	173·43	3·09
Ethyl bromide	0	1·45983	172·6*	−0·95*
	2·01598	1·45333	172·41	—
	4·9815	1·44395	172·26	−0·98
	0‡	1·46018		
	10·92	1·42631	171·75	−1·05
	30·576	1·37055	171·25	−0·52
	65·282	1·28272	170·97	+2·73
Ethylene bromide	0	2·1816	—	−18·8*
	5·58716	2·08023	176·78	−14·3
Acetylene tetrabromide.........	0	2·9638	176·8*	−20·0*
	5·6676	2·72804	175·49	−13·47
	9·95956	2·57561	174·69	−10·19
	20·1106	2·27798	173·56	−5·53
Methyl iodide.....................	0	2·27899	179·8*	1·08*
	5·19605	2·17005	177·77	1·13
	10·4466	2·07288	176·42	1·20
	38·0809	1·68698	173·67	2·85
Methylene iodide	0	3·32537	—	—
	1·4233	3·23921	177·7	−0·8
Ethyl iodide	0	1·93706	178·3*	−2·2*
	5·17118	1·87279	176·9	−1·88
	10·6333	1·81155	175·6	−1·46
	32·766	1·6044	173·6	+0·24

* Extrapolated. † See note on p. 367.

‡ A fresh sample of ethyl bromide was used for the next three solutions.

It gives us pleasure, in conclusion, to acknowledge our indebtedness to the Research Fund Committee of the Chemical Society for a grant, which defrayed the expenses of this investigation.

THE UNIVERSITY, GLASGOW.

XXXVI.—*The Refractive Power of Diphenylhexatriene and Allied Hydrocarbons.*

By Ida Smedley.

The present investigation was undertaken three years ago with the object of studying the refractive powers of open-chain hydrocarbons containing contiguous ethenoid groups. The molecular refractive power of benzene had been regarded as evidence that benzene contained three ethylene linkings (Brühl, *Ber.*, 1887, **20**, 2288); it was therefore important to determine the effect of three contiguous ethenoid groups arranged in an open-chain.

The phenyl radicle was known to exert an increased influence in cinnamyl compounds; the exact conditions affecting this variation, however, had not been clearly defined. It was important to ascertain whether the mere accumulation of phenyl groups involved a disproportionate increase of refractive power or whether such increase took place only when phenyl was connected with an unsaturated group. Evidence was required as to whether any sudden change takes place in refractive power when phenyl is associated with an unsaturated group, such as might be expected if the phenyl radicle were to change suddenly from an ethenoid to a centric condition; or whether the change is a gradual one and the order of increase in any way proportionate to the number of unsaturated groups associated with the benzenoid structure.

Finally, additional evidence was needed as to the influence of unsaturated groups on each other. Does a series of unsaturated groups act as a conducting chain, in such a manner that the addition of an unsaturated group at one point of the chain influences the refractive power of each unsaturated group present or is the effect of the newly-added radicle limited only to the adjacent groups?

I had already been some time engaged in preparing the simplest hexatriene, $CH_2\colon CH \cdot CH\colon CH \cdot CH\colon CH_2$ (Proc., 1906, **22**, 158), when its synthesis was accomplished by van Romburgh and van Dorssen (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, **8**, 565); the refractive and magnetic rotatory powers of the hydrocarbon were subsequently ascertained by Sir William Perkin (Trans., 1907, **91**, 806). To synthesise diphenylhexatriene, $C_6H_5 \cdot CH\colon CH \cdot CH\colon CH \cdot CH\colon CH \cdot C_6H_5$, the attempt was made to eliminate chlorine from αα-dichloro-γ-phenylpropylene, $C_6H_5 \cdot CH\colon CH \cdot CHCl_2$, but without success; the diformate of dihydrocinnamoin was then prepared, and examined in the hope that diphenylhexatriene would be formed on distilling this compound.

Dihydrocinnamoin.—This compound was prepared by reducing cinnamaldehyde, dissolved either in glacial acetic acid or in alcohol, by means of zinc dust; at most, 10 per cent. of the theoretically possible amount was obtained; no other product could be isolated from the viscous solution (compare Thiele, *Ber.*, 1899, **32**, 1296).

On warming dihydrocinnamoin with an alcoholic solution of silver nitrate, a silver mirror is at once formed; dihydrobenzoin has a similar effect, but acts very much more slowly. Apparently, the reducing power of the secondary alcohol group is affected by the presence of the conjoined ethenoid group much as it is by that of a carbonyl group. In fructose, the reducing power of one of the secondary alcohol groups was ascribed by Fischer to the influence of the adjacent carbonyl group. In dihydrobenzoin, the influence of phenyl is to increase the reducing character of the CH·OH group; this effect appears to be further heightened when the phenyl is displaced by the more unsaturated cinnamyl group.

In the hope of obtaining an osazone, dihydrocinnamoin was heated with phenylhydrazine acetate; the liquid quickly became deep red, a small amount of a dark red oil separating, but the greater part of the original compound was recovered unchanged; no other substance could be isolated.

Action of Formic Acid on Dihydrocinnamoin.

Eleven grams of dihydrocinnamoin were heated with 20 c.c. of formic acid (D 1·2) during four hours on a water-bath. A deep yellow oil separated, which solidified to a hard, yellow, resinous mass, approximating in composition to the diformate of dihydrocinnamoin. It was readily soluble in organic solvents but was deposited always as a yellow oil, which solidified gradually to a resinous mass.

The difficulty experienced in purifying this substance, its tendency to resinify, together with the small yield of dihydrocinnamoin originally obtained, induced me to seek another means of preparing diphenylhexatriene; eventually, it was found that it could be prepared by condensing cinnamaldehyde with phenyl*iso*crotonic acid (Proc., 1907, **23**, 162):

$$C_6H_5{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CO_2H + CHO{\cdot}CH{:}CH{\cdot}C_6H_5 = \\ CO_2 + H_2O + C_6H_5{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}C_6H_5.$$

Condensation of Phenylisocrotonic Acid with Cinnamaldehyde.

A mixture of molecular proportions of sodium phenyl*iso*crotonate, cinnamaldehyde, and acetic anhydride was heated during forty minutes on an oil-bath at 140°. A clear yellow liquid was obtained, which solidified on cooling. In the first experiment, the mass was extracted with a solution of sodium carbonate, which was then shaken with ether. Between the two layers, an extremely small amount of small, yellow, glistening leaves separated but no other substance could be isolated; the crude product consisted mainly of resinous substances of indefinite composition, similar to those obtained in preparing dihydrocinnamoin.

If the crude product be not first treated with sodium carbonate, but at once extracted with boiling chloroform or acetone, yellow, glistening leaves are deposited from the liquid on cooling, the yield being considerably increased. From 35 grams of phenyl*iso*crotonic acid, 2 grams of the hydrocarbon were thus obtained.

After this preliminary purification, the hydrocarbon may be treated with sodium carbonate without diminishing the yield; it was finally recrystallised several times from boiling acetone and chloroform respectively, the melting point was 194° (uncorr) :*

0·0618 gave 0·2100 CO_2 and 0·0404 H_2O. $C = 92·72$; $H = 7·28$
0·1354 „ 0·4602 CO_2 „ 0·0880 H_2O. $C = 92·69$; $H = 7·22$.
$C_{18}H_{26}$ requires $C = 93·10$; $H = 6·90$ per cent.

Action of Bromine.—To a solution of 0·5 gram of the hydrocarbon in chloroform, three molecular proportions of bromine dissolved in the same solvent were added. The yellow solution was decolorised at first, but eventually became coloured by the bromine. After some time, a white solid separated, which, when recrystallised from chloroform, appeared in rather indefinite needles, melting, but decomposing, at 228—230° (uncorr.). This substance was *diphenylhexatriene hexabromide*:

0·0989 gave 0·1578 AgBr. $Br = 67·89$.
$C_{18}H_{16}Br_6$ requires $Br = 67·42$ per cent.

The very dilute solution in chloroform or benzene of diphenylhexatriene shows a beautiful blue fluorescence, which gradually disappears, the solution acquiring a brown tinge.

The pale yellow colour appears to be an inherent property of the hydrocarbon, as it is not removed by continued recrystallisation. This is the lowest member of this series of hydrocarbons in which colour appears; diphenylbutadiene, $C_6H_5·CH:CH·CH:CH·C_6H_5$, prepared according to Thiele's method (*Annalen*, 1899, **306**, 201), is a white substance, showing a marked blue fluorescence in alcoholic solution, but both diphenylhexatriene and diphenyloctatetrene (Fittig, *Annalen*, 1904, **331**, 151) are yellow.

Determinations of Refractive Index.—The high melting points of these substances and their comparative insolubility make the determination of their refractive power difficult. The best solvent for diphenylhexatriene is chloroform, but at the ordinary temperature a saturated solution contains less than 2 per cent., and even at the boiling point a chloroform solution contains less than 4 per cent. The refractive power of the diphenyl derivatives of butadiene and hexatriene was determined in dilute chloroform solutions (1 to 3 per cent.); to check the results, diphenyl and benzene were examined under similar conditions, and the results compared with the values obtained by other observers' work with the undiluted substances.

---

* Since completing this work, I have learnt that the same condensation has been studied in Professor Thiele's laboratory by Knell, who has isolated diphenylhexatriene-γ-carboxylic acid by working at lower temperatures, and has obtained about 0·5 gram of the hydrocarbon as the result of fifteen to twenty condensations (*Inaug. Diss.*, Munich, 1902).

The experimental error arising from the use of such dilute solutions appears to be about 2 per cent.; but the refractive power is so much higher than that calculated, using the values deduced from fatty compounds, that this degree of error does not seriously affect the conclusions to be drawn. The error is exaggerated in calculating the dispersive powers, which are therefore less trustworthy than the refractive powers; the numbers indicate, however, that a very remarkable increase in dispersive power attends the introduction of every additional unsaturated group (compare Brühl, *Ber.*, 1907, **40**, 878, 1153).

The very slight solubility of the octatetrene derivatives makes them still less suitable for examination.

The *chloroform* used as a solvent in the first set of experiments was dried over calcium chloride and distilled, the portion boiling from 61·3° to 61·5° being collected. The specimen used in later experiments was freed from alcohol by washing several times with water, then allowed to stand over concentrated sulphuric acid, and finally distilled from potassium carbonate.

Diphenylhexatriene.—The preparation and purification of this hydrocarbon have already been described.

Diphenylbutadiene.—This was prepared and purified according to the directions given by Thiele (*Annalen*, 1899, **306**, 201).

Diphenyl.—The specimen used was obtained from Kahlbaum; it melted at 71°.

Benzene.—This was dried over calcium chloride, then allowed to stand over phosphoric oxide, distilled from this, and carefully fractionated.

The observations were made with a Pulfrich refractometer at temperatures lying between 15° and 20°; the specific refractive powers of the solutions examined are given in table I:

TABLE I.

Substance.	Formula.	Per cent. strength of solution.	$\frac{\mu_\alpha^2-1}{(\mu_\alpha^2+2)}\cdot\frac{1}{d}$.	$\frac{\mu_\beta^2-1}{(\mu_\beta^2+2)d}$.	M_α.	M_β.	$M_\beta - M_\alpha$.
Chloroform:							
Specimen I	$CHCl_3$	—	0·17848	0·18157	21·23	21·70	0·37
Specimen II used in 2nd determination diphenylhexatriene		—	0·17831	0·18145	21·30	21·68	0·38
Benzene	C_6H_6	1·3029	0·18158	—	26·0	—	—
Diphenyl	$C_{12}H_{10}$	3·0062	0·18334	0·18668	52·35	54·15	1·8
Diphenylbutadiene .	$C_{16}H_{14}$	4·4493	0·18821	0·19324	81·86	91·44	9·5
		1·8132	0·18264	0·18644	83·96	92·70	8·8
Diphenylhexatriene .	$C_{18}H_{16}$	1·238	0·18159	0·18553	99·7	116·4	16·7
		1·1744	0·18138	0·18545	102·1	121·2	19·1

Influence of the Phenyl Radicle in Saturated Hydrocarbons.

The effect of the successive displacement of the hydrogen atoms of methane by the phenyl radicle was studied by Sir William Perkin, who concluded that, using the formula $\frac{\mu-1}{d}$ for the specific refraction, the increment in refractive power increases slightly with the introduction of each additional phenyl group (Trans., 1895, **69**, 1152). If, however, the formula $\frac{\mu^2-1}{\mu^2+2}\cdot\frac{1}{d}$ be applied, the agreement between the numbers obtained is well within the limits of experimental accuracy, unavoidable error being introduced by our reference to an arbitrarily chosen standard, such as the red hydrogen line.

Table II shows that the value for the introduction of the phenyl group into a fatty hydrocarbon is unaffected by the subsequent introduction of a phenyl radicle, both where the phenyl groups are united with the same carbon atom and where they are separated by saturated hydrocarbon groups.

TABLE II.

Observer.	Substance.	Formula.	Temp. at which examined.	$\frac{M}{d}\cdot\frac{\mu_\alpha^2-1}{\mu_\alpha^2+2}$.	Increment
Dulong	Methane	CH_4	0°	6·61 *	—
Mascart......				6·62	—
Perkin	Toluene	$CH_3{\cdot}C_6H_5$	99	31·08	24·46
Perkin	Diphenylmethane	$CH_2(C_6H_5)_2$	99	55·38	24·30
Perkin	Triphenylmethane	$CH(C_6H_5)_3$	99	79·82	24·44
	Ethane	$CH_3{\cdot}CH_3$	—	—	—
Landolt and Jahn	Ethylbenzene......	$CH_3{\cdot}CH_2{\cdot}C_6H_5$	14·5	35·33	—
Eyckmann..	Dibenzyl	$C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5$	80·6	60·07	24·27
Chilesotti ...			20 (in solution)	59·6†	

---

* This value is for sodium light, but the degree of dispersion in such a compound is so small that the value is very little affected.

† The lower number is taken, since, if the temperature-coefficient be taken into account, the other value would be appreciably diminished.

Influence of the Phenyl Radicle in Unsaturated Hydrocarbons.

As early as 1881, Gladstone pointed out that the refractive power of substances in which an unsaturated group is joined to phenyl is abnormally high (*Proc. Roy. Soc.*, 1881, **31**, 327); subsequently, it was shown by Brühl that, not only is the refractive power of cinnamyl compounds greater than the calculated value, but that the molecular refractive powers of isomeric compounds in which two ethenoid linkings occurred was not identical. Of the three structures, $\cdot CH\colon CH\cdot CH\colon CH\cdot CH_2\cdot$ $\cdot CH\colon C\colon CH\cdot CH_2\cdot CH_2\cdot$ $\cdot CH\colon CH\cdot CH_2\cdot CH\colon CH\cdot$ the first alone exhibited an abnormally high refractive power (Brühl, *Annalen*, 1886, **235**, 56; *Zeitsch. physikal. Chem.*, 1891, **7**, 2), the increase being always accompanied by abnormal dispersive power.

The combined effect of ethenoid groups forms the basis of the quinonoid theory of colour, and, in his advocacy of this theory, Professor Armstrong has for many years brought forward the view that contiguous ethenoid groups mutually influence each other, co-operating to produce a selective absorption of light. This same idea of the mutual influence of unsaturated groups was applied by him to explain the abnormally high refractive power of certain benzenoid aldehydes (Proc., 1893, **9**, 57).

Subsequently, this idea of the mutual influence of alternately arranged ethylene linkings gained further support from Thiele's work (*Annalen*, 1899, **306**, 87).

A large number of data have now been accumulated, showing that the presence of unsaturated groups in conjunction in the molecule always increases both the refractive and the dispersive power; Brühl (*Ber.*, 1907, **40**, 878, 1153) suggests that the effect of the conjugation is not merely a qualitative but a quantitative one, and will be found to depend both on the kind and on the number of groups present in conjunction.

A contribution to our knowledge of the influence of the phenyl group has been made by Chilesotti, who has examined hydrocarbons such as anthracene and phenanthrene, and interpreted his results as supporting the centric formula for benzene (*Gazzetta*, 1900, **30**, i, 149).

Tables III, IV, and V show that the effect of the phenyl group in unsaturated hydrocarbons depends on the number and the nature of the other unsaturated groups present in the molecule. The increment in refractive power increases gradually where the phenyl group is united with an ethenoid or a second phenyl group and reaches its maximum value where it acts in conjunction with a chain of contiguous ethenoid groups linked to a second phenyl nucleus as in diphenyhexatriene.

TABLE III.

Substance.	Mol. refraction for H_a.	Increment.	Substance.	M_a.	Increment.	Substance.	M_a.	Increment.
Hydrogen, H·H·	2·11 [1]	—	Benzene, Ph·H	25·93 [4]	—	Diphenyl, Ph·Ph	51·93 [7]	—
Ethylene, HC:CH H H	10·77 [2]	8·66	Cinnamene, Ph·C:CH H H	35·98 [5]	10·05	Stilbene, Ph·C:CPh H H	65·65 [8]	13·7
Butadiene, HC:C·C:CH H H H H	—	—	Phenylbutadiene, PhC:C·C:CH H H H H	48·00 [6]	12·02	Diphenylbutadiene, PhC:C·C:CPh H H H H	82·9	17·2
Hexatriene, HC:C·C:C·C:CH H H H H H H	30·58 [3]	19·8/2	Phenylhexatriene, PhC:C·C:C·C:CH H H H H H H	—	—	Diphenylhexatriene, PhC:C·C:C·C:CPh H H H H H H	100·9	18·0
						Diphenyloctatetrene, PhC:C·C:C·C:C·C:CPh H H H H H H H H	—	—

---

[1] Ketteler, *Zeitsch. physikal. Chem.*, 1891, **7**, 25.

[2] Liveing and Dewar, *Phil. Mag.*, 1892, [v], **34**, 209.

[3] Perkin. Trans., 1907, **91**, 815.

[4] Brühl, *Zeitsch. physikal. Chem.*, 1891, **7**, 181.

[5] Brühl, *loc. cit.*

[6] Klages, *Ber.*, 1907, **40**, 1768.

[7] Eyckmann, *Rec. trav. chim.*, 1893, **12**, 157.

[8] Chilesotti, *loc. cit.*

TABLE IV.

Increment in Refractive Power on introducing an Ethenoid Group.

Ethylene – Hydrogen HC:CH – H·H H H	10·77 – 2·10	(1) Between two hydrogen atoms.	8·67
Hexatriene – Hydrogen HC:C·C:C·C:CH – H·H H H H H H H	$\frac{30{\cdot}58 - 2{\cdot}10}{3}$	(2) Between two hydrogen atoms when three ethenoid groups are present.	9·49
Cinnamene – Benzene Ph·C:CH – Ph·H H H	35·98 – 25·93	(3) Between a hydrogen atom and a phenyl group.	10·05
Phenylbutadiene – Benzene PhC:C·C·CH – Ph:H H H H H	$\frac{48{\cdot}00 - 25{\cdot}93}{2}$	(4) Between a hydrogen atom and a phenyl group when two ethenoid groups are present.	11·03
Stilbene – Diphenyl PhC:CPh – Ph·Ph H H	65·65 – 51·95	(5) Between two phenyl groups.	13·70
Diphenylbutadiene – Diphenyl PhC:C·C:CPh – Ph·Ph H H H H	$\frac{82{\cdot}9 - 51{\cdot}95}{2}$	(6) Between two phenyl groups when two ethenoid groups are present.	15·5
Diphenylhexatriene – Diphenyl PhC:C·C:C·C:CPh – Ph·Ph H H H H H H	$\frac{100{\cdot}9 - 51{\cdot}95}{3}$	(7) Between two phenyl groups when three ethenoid groups are present.	16·3

TABLE V.

Increment in Refractive Power on displacing a Hydrogen Atom by the Phenyl Group.

Benzene – Hydrogen Ph·H – H·H	25·98 - 2·10	(1) United to a single hydrogen atom.	23·88
Cinnamene – Ethylene PhC:CH – H·C:CH H H H H	35·98 – 10·77	(2) United to an ethenoid group.	25·21
Diphenyl – Hydrogen Ph·Ph – H·H	$\frac{51{\cdot}95 - 2{\cdot}10}{2}$	(3) United to a phenyl group.	24·92
[Diphenyl – Benzene = 26·03 Ph·Ph – Ph·H]			
Stilbene – Ethylene PhC:CPh – HC:CH H H H H	$\frac{65{\cdot}65 - 10{\cdot}77}{2}$	(4) United to a cinnamyl group.	27·44
[Stilbene – Cinnamene = 29·67 PhC:CPh – PhC:CH H H H H]			
[Diphenylbutadiene – Phenylbutadiene = 34·9 PhC:C·C:CPh – PhC:C·C:CH H H H H H H H H]			
Diphenylhexatriene – Hexatriene PhC:C·C:C·C:CPh – HC:C·C:C·C:CH H H H H H H H H H H H H	$\frac{100{\cdot}9 - 30{\cdot}58}{2}$	(5) United to one phenyl and three ethenoid groups.	35·2

On comparing the values thus obtained, it is seen that the insertion of three ethenoid groups between two phenyl nuclei produces an increment of 47·4 units in the molecular refractive power, whereas the insertion of three similar groups between two hydrogen atoms only raises it by 28·5 units. Part of the former increase is therefore due to the influence of the phenyl groups, but the effect produced by these does not remain of constant value, as it is heightened by association with unsaturated groups, and this increase, together with that due to the ethenoid groups in conjunction, is measured when the molecular refractive power of diphenyl is subtracted from that of diphenylhexatriene. The relative influence of the phenyl and ethenoid groups may, however, be calculated as follows:

Assuming that the two hydrogen atoms at the ends of the chain have the same value as in the hydrogen molecule:

Molecular refractive power of hydrogen	2·10
Refraction increment on displacing two hydrogen atoms by two phenyl radicles associated with three contiguous ethenoid groups (M_a-diphenylhexatriene − M_a-hexatriene)	70·3
Increment on inserting three ethenoid groups between two phenyls (M_a-diphenylhexatriene − M_a-diphenyl)	48·9
	121·3

The observed refractive power of diphenylhexatriene is, however	100·9
The value for each ethenoid group should therefore be $\frac{1009}{1213} \times \frac{48 \cdot 9}{3}$.	13·55
For each phenyl displacing hydrogen, $\frac{1009}{1213} \times \frac{70 \cdot 3}{2}$	29·33

Similarly, the increment caused by the insertion of a single ethenoid group between two phenyls may be calculated:

Molecular refractive power of hydrogen	2·10
Increment on displacing two hydrogen atoms by two phenyls, M_a-stilbene − M_a-ethylene	54·88
Increment on inserting one ethenoid group between two phenyls, M_a-stilbene − M_a-diphenyl	13·70
	70·68

The molecular refractive power of stilbene is, however	65·65
∴ The value for the ethenoid group should be $\frac{65 \cdot 65}{70 \cdot 68} \times 13 \cdot 70$	12·72
For the displacement of hydrogen by phenyl, $\frac{65 \cdot 65}{70 \cdot 68} \times 27 \cdot 44$	25·48

A similar correction may be made when one phenyl is associated with one ethenoid group:

M_a-hydrogen	2·10
Cinnamene − benzene	10·0
Cinnamene − ethylene	25·21
	37·31

Molecular refraction of styrene .... 35·98

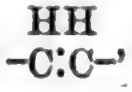
∴ Value for the ethenoid group, $\frac{35 \cdot 98}{39 \cdot 21} \times 10$ .... 9·64

Value for the displacement of hydrogen by phenyl, $\frac{35 \cdot 98}{37 \cdot 31} \times 25 \cdot 21$ ... 24·31

Summarising these results :

Increment in molecular refractive power caused by the displacement of a hydrogen atom by phenyl when it is joined to :

(*a*)	A hydrogen atom	23·88
(*b*)	A saturated hydrocarbon radicle	24·40
*(*c*)	An ethenoid group	24·31
(*d*)	A phenyl group	24·94
(*e*)	A cinnamyl group	25·48
(*f*)	A phenyl group in conjunction with three ethenoid groups	29·23

Increment owing to the introduction of an ethenoid group,  $\overset{H}{-C}\overset{H}{:C}-$, *into the molecule between* :

(*a*)	Two hydrogen atoms	8·67
(*b*)	Two ethenoid groups	9·50
(*c*)	A hydrogen and a phenyl group	9·64
(*d*)	Two phenyl groups	12·72
(*e*)	Two phenyl groups where three ethenoid groups are in conjunction	13·55

Both the phenyl radicle and the ethenoid group exercise a gradually increasing influence on the refractive power, and this increase depends on the number of unsaturated groups with which each is associated, the maximum effect being reached in diphenylhexatriene. The carbon atoms in the ethenoid group are more affected by association with unsaturated groups than the carbon atoms of the phenyl nucleus. This is shown both by the high refractive power of hexatriene as compared with benzene, and by the greater rate of increase in the ethenoid as compared with the phenyl group.

As we do not know whether the atomic refractive powers of the carbon and hydrogen atoms increase in the same proportion, it is desirable at present to deal rather with groups of atoms, the effect of which is directly measurable than with the atomic refractive powers.

The numbers thus obtained are applicable only to substances which contain no other kind of unsaturated group in the molecule, the presence, for instance, of a contiguous carbonyl group causing a readjustment of values.

---

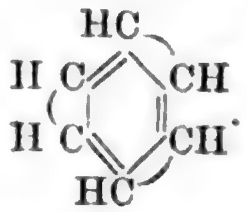
* It will be seen that the influence of phenyl on the ethenoid group is much more marked than is the converse effect. The effect of a single such group distributed over a whole phenyl nucleus, is probably so slight as to be within the limit of experimental error.

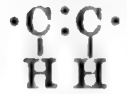
Conclusions.

There is apparently a close parallelism between the atomic structures which condition colour and those producing increased refractive power, for in both cases the presence of conjoined unsaturated groups appears to be essential. In ascending the series of hydrocarbons, diphenyl, diphenylethylene, diphenylbutadiene, and diphenylhexatriene, the refractive increment produced by each phenyl and each $\cdot C_2H_2\cdot$ group increases steadily. Solutions of diphenylbutadiene show a blue fluorescence, which is more marked in the higher members of the series, but it is only on reaching diphenylhexatriene that visible colour makes its appearance.*

A study of the refractive power of these unsaturated hydrocarbons affords striking confirmation of the mutual influence of unsaturated groups. A method of numerical comparison of the influence exerted by the different radicles appears to be available, which shows that the successive introduction of each unsaturated group into the molecule influences the whole series of unsaturated groups as long as they are in conjunction; the refractive power of each unsaturated group already present is increased by the introduction of the new unsaturated group.

The striking difference in the refractive power of hexatriene and of benzene itself (the loss of two hydrogen atoms and the closing of the ring being accompanied by a diminution of as much as five units) makes the effect on the refractive power produced by the phenyl nucleus of special interest. Originally, the molecular refractive power of benzene was regarded as evidence that the benzene molecule contained three ethylene linkings, since it exceeded the value calculated for six carbon and six hydrogen atoms by three times the value assigned to one double bond (Brühl, *Ber.*, 1887, **20**, 2288). According to Thiele's theory, the benzene molecule consists of three conjoined unsaturated groups, which, since they are joined in a ring, possess no free partial valencies, the structure being represented by the formula



In open-chain compounds, however, the refractive power of  $\cdot\underset{H}{C}:\underset{H}{C}\cdot$ groups in conjunction is higher than that of a single unsaturated radicle, and increases with the number of conjoined groups. It would be expected, therefore, that if this structure really represented the benzene molecule, its refractive power would be abnormally high, since the groups possess no free partial valencies, and are more compactly united than in an open-chain structure. Brühl now regards the phenyl nucleus as existing in two states, the "neutral conjugated" condition—where the unsaturated groups do not behave as if they were conjoined—and the "active conjugated" condition—in which, assuming that the benzene molecule contains unsaturated groups, these show increased values similar to those observed in open-chain conjoined systems (*Ber.*, 1907, **40**, 878).

---

* It is interesting, however, that the association of two adjacent carbonyl groups does not appreciably increase the refractive index, although it is sufficient to produce colour.

The assumption that the benzene nucleus contains three ethylene linkings has not proved to be in accordance with the evidence as to its refractive power; any method of calculation based on this assumption may therefore be misleading. Regarding the phenyl nucleus as a whole, we see that, whatever the change which occurs in it influencing its refractive value, it is a gradual change, very slightly increasing as one unsaturated group is joined to it but continuing to increase in value as each successive unsaturated group is associated with it. The very gradual character of this increase seems to me to deter us from regarding the change produced as a sudden change from a condition of neutral to one of active conjunction; it appears to be more in accordance with a structure represented by the centric formula, which assumes that the arrangement of forces obtaining between the carbon atoms of the benzene nucleus differs from that holding in open-chain structures, whether saturated or unsaturated.

The influence of the phenyl nucleus on the magnetic rotation of aromatic compounds agrees very closely with that of three ethenoid groups conjoined in an open-chain structure, the increase in magnetic rotatory power produced by each of these structures being comparable. As far as this property is concerned, the relations between hexatriene and benzene are similar to those between hexane and hexamethylene (Perkin, Trans., 1907, **91**, 806). The introduction of successive phenyl groups into an alkyl radicle produces a much more marked effect than on the refractive power. Close as is the parallelism generally holding between the structures producing increments in the atomic refractive and magnetic rotation values of the elements, the benzene nucleus furnishes a marked exception. Whereas, from its magnetic rotation value, it appears to be closely connected with an open-chain structure, containing three contiguous ethenoid groups, its refractive power points to a degree of unsaturation intermediate between that of a fatty saturated compound and of a hexatriene structure, a result more closely in agreement with its chemical behaviour. Our present incomplete knowledge does not enable us to reconcile the conflicting aspects, shown to us by its influence on light absorption, light refraction, and magnetic rotation.

The determinations of the refractive index were made at the Manchester Municipal School of Technology, and I desire to acknowledge my thanks to Professor Pope for permission to use the instruments in that laboratory.

VICTORIA UNIVERSITY,
MANCHESTER.

XXXVII.—*The Temperatures of Spontaneous Crystallisation of Mixed Solutions and their Determination by Means of the Index of Refraction. Mixtures of Solutions of Sodium Nitrate and Lead Nitrate.*

By FLORENCE ISAAC, Research Fellow of Somerville College.

EXPERIMENTS on the refractive indices of certain simple solutions of salts in water (Trans., 1906, **89**, 413) have led to the determination of a "supersolubility curve" which gives the temperature of spontaneous crystallisation for the various solutions, and therefore marks the passage of a supersaturated solution from the metastable to the labile condition if we adopt the phraseology of Ostwald.

The object of the present paper is to investigate the refractive indices of mixed solutions of two salts A and B in water, and so to determine the supersolubility curves for a mixture of three substances, namely, salt A, salt B, and water; the salts chosen were lead nitrate and sodium nitrate.

Two complete sets of experiments were undertaken. In the first set the proportion of lead nitrate to water was kept constant, and the amount of sodium nitrate varied; and in the second set the proportion of sodium nitrate to water was kept constant and the amount of lead nitrate varied.

The method of experimenting was the same as that described in the previous paper, which dealt with simple solutions. The hot mixed solution was placed in an open trough beneath the inverted goniometer described by Prof. Miers (*Phil. Trans.*, 1903, *A*, **202**, 464), and the refractive indices were determined from time to time as it cooled by means of an immersed glass prism by the method of total internal reflection. The solutions were kept stirred rapidly by means of a platinum vane driven by an electric motor.

In some of the experiments a new goniometer specially designed for these experiments was employed. In principle this instrument much resembles the one referred to above, but has the following advantages: a larger amount of solution can be employed; greater accuracy of measurement is possible; the second support of the disc, which prevented the free movement of the telescope and its adjustment in line with the collimator, is done away with; and the solution can be kept at a constant temperature for any desired period. The collimator is fixed in the single vertical leg of the instrument, which rises from the base and supports the horizontal graduated disc of the goniometer. The telescope can thus be moved almost completely round the goniometer axis. The prism holder is furnished with the usual centring and adjusting screws, and the prism is held by a platinum clip. Below the prism holder and on a table supported by the base of the instrument is a large circular glass trough, which can be raised or lowered by means of a rack and pinion. This trough contains the solution, the suspended prism being immersed in it. The front of the trough is a plane-parallel glass plate, held in position by clips, and the table which carries the trough is furnished with levelling screws so that it can be adjusted and the glass front set perpendicular to the telescope axis.

A circular metal tube provided with holes on the inner side fits over the upper rim of this trough; hot or cold water may be passed through this tube, and, issuing from the holes, streams over the outer surface of the trough and is carried away through an aperture in the table. The solution can thus be maintained at a constant temperature.

The capacity of the trough is 325 c.c., so that much larger quantities of solution can be examined than was possible with the goniometer previously used. The solutions were thoroughly stirred by means of a glass plunger bent in the shape of a horse-shoe with its open end opposite to the plane glass front; and an up-and-down movement is given to the stirrer by means of a crank clamped to the leg of the goniometer and driven by a small electric motor. The graduated circle divided to 10″ is read by means of two attached verniers and small lenses.

First Set of Experiments. Solutions containing Excess of Sodium Nitrate in which the Proportion of Lead Nitrate to Water was 3 : 10.

The amount of sodium nitrate varied from 42 to 49·5 per cent. of the whole solution.

The solutions were placed in the goniometer trough at about 60° or 70°, and the change in the refractive index was traced until the temperature had fallen to 18° or 15°. Throughout this set of twenty-two experiments, sodium nitrate alone crystallised out of the solutions.

The results of some of these experiments are shown in Fig. 1, on which are plotted the variations of refractive index with concentration and temperature. The first eleven of the experiments were carried out in an open trough, so that evaporation from the surface of the liquid was not prevented. The concentration of the solutions must, from this cause, have increased slightly throughout these experiments. In the remaining eleven experiments the solutions were also introduced into the trough at about 60° or 70°, but were immediately covered with a layer of olive oil at the same temperature. This layer prevented evaporation, and in these eleven experiments, therefore, the concentration was constant until crystals began to appear in the trough.

From these last experiments curves of constant refractive index were plotted on a concentration-temperature diagram. The curves were found to be approximately straight lines parallel to each other, and inclined at an angle of 46° 41′ to the temperature axis for the scale chosen, on which 1 per cent. of sodium nitrate corresponds with 5°. These constant index lines are shown in Fig. 1, and if a line be drawn at right angles to them inclined at an angle of 43° 19′ to the temperature axis, equal lengths measured along this line correspond with equal changes in refractive index.

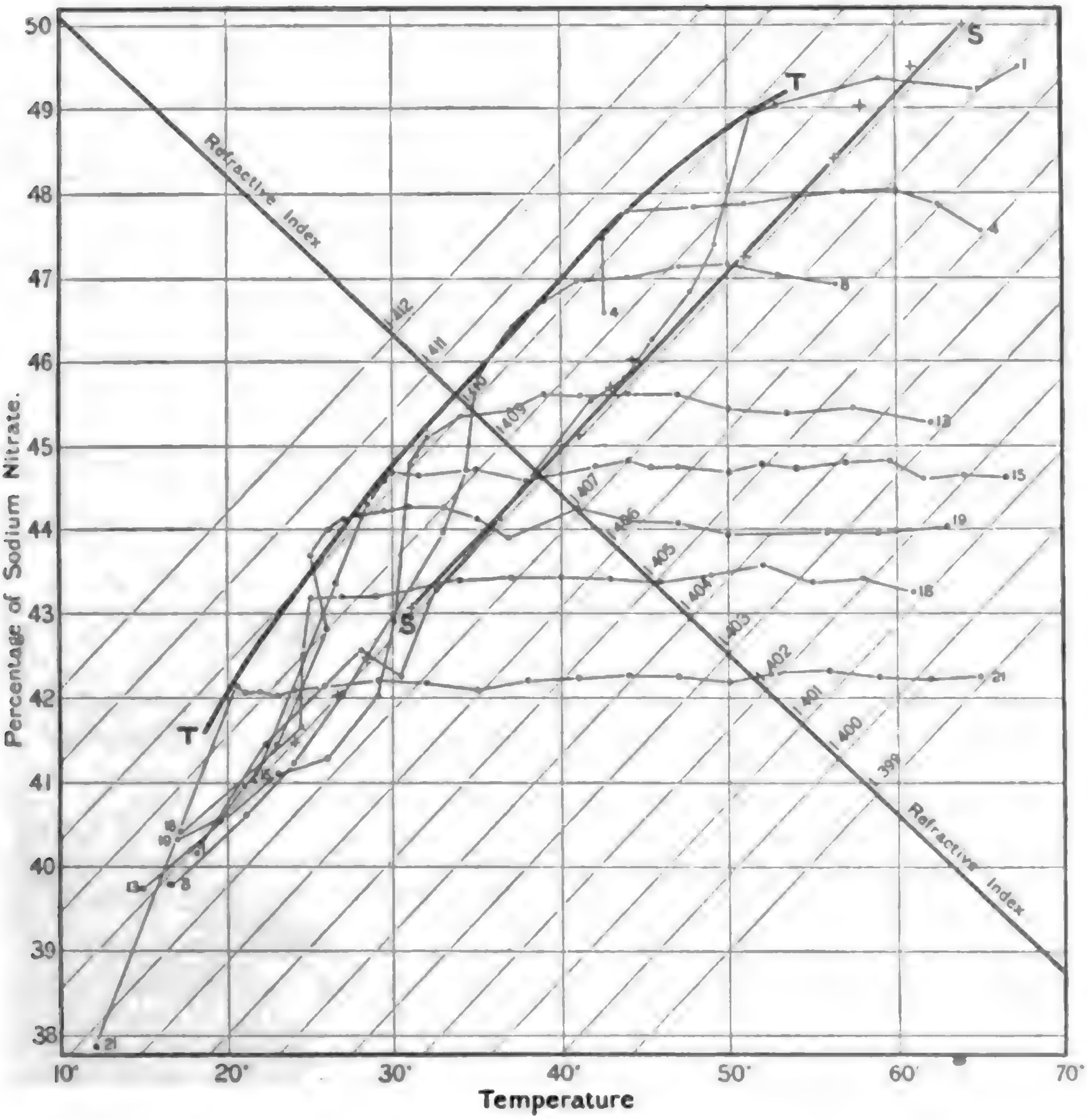
It is therefore possible to indicate the changes in the refractive indices of the solutions as they cool, by distances measured along such a line, in the same way that changes of temperature are measured along the horizontal axis. The curves in Fig. 1 showing the behaviour of the mixed solutions are all plotted from the refractive indices measured along this line, and from the temperature measured along the horizontal axis. The ordinates give the concentrations of the solutions at any temperature.

Description of Curves in Fig. 1.

It will be seen from Fig. 1 that in general the index of the solutions rises at first fairly rapidly as the temperature falls. There is sometimes a slight depression in the curves as they cross the solubility curve *S*, after which the concentration falls a little. The refractive index, however, continues to rise until it reaches a maximum value, after which it suddenly begins to fall again, slowly at first and then rapidly, owing to the weakening of the solution when spontaneous crystallisation sets in, until the curves ultimately approximate to the solubility curve *S*.

As with the simple solutions already examined, it will be seen from Fig. 1 that at the points where the solutions attain their highest refractive indices all the curves approximately touch a continuous curve. This curve, *T*, is the supersolubility curve for the set of mixtures containing from 42 to 49·5 per cent. of sodium nitrate in a solution of lead nitrate and water, the proportion of lead nitrate to water being 3 : 10.

FIG. 1.



Between 20° and 40° the supersolubility curve is approximately a straight line, but above 40° it bends towards the solubility curve *S*, and indicates that the metastable region for the stronger solutions becomes rapidly narrower at higher temperatures.

Behaviour of Mixed Solutions compared with that of Simple Solutions.

The results obtained from the experiments with mixed solutions as they cool resemble those obtained from simple solutions. The refractive index rises to a maximum. As soon as, or very shortly after, the maximum index is reached, a dense shower of sodium nitrate crystals appears throughout the solution, rendering it almost opaque.

The behaviour of these mixtures only differs from that of simple solutions in that for the more concentrated mixtures of this series, that is, those containing from 45 to 49·5 per cent. of sodium nitrate, when stirred in an open vessel, a very fine shower of sodium nitrate crystals appears suddenly in the solution in the metastable region before the maximum index is reached, in addition to the dense shower of crystals which appears at the maximum point and the few isolated crystals which appear at or about the temperature of saturation.

Also, after the maximum index is attained, the fall is continuous until a certain temperature, after which the change of index is sometimes oscillatory. The index then usually remains approximately constant for some time, and finally rises again slightly. This behaviour is well shown in experiments 1, 2, 5, 8, 9 (compare Fig. 2).

The following are the tabulated results for the set of experiments described above.

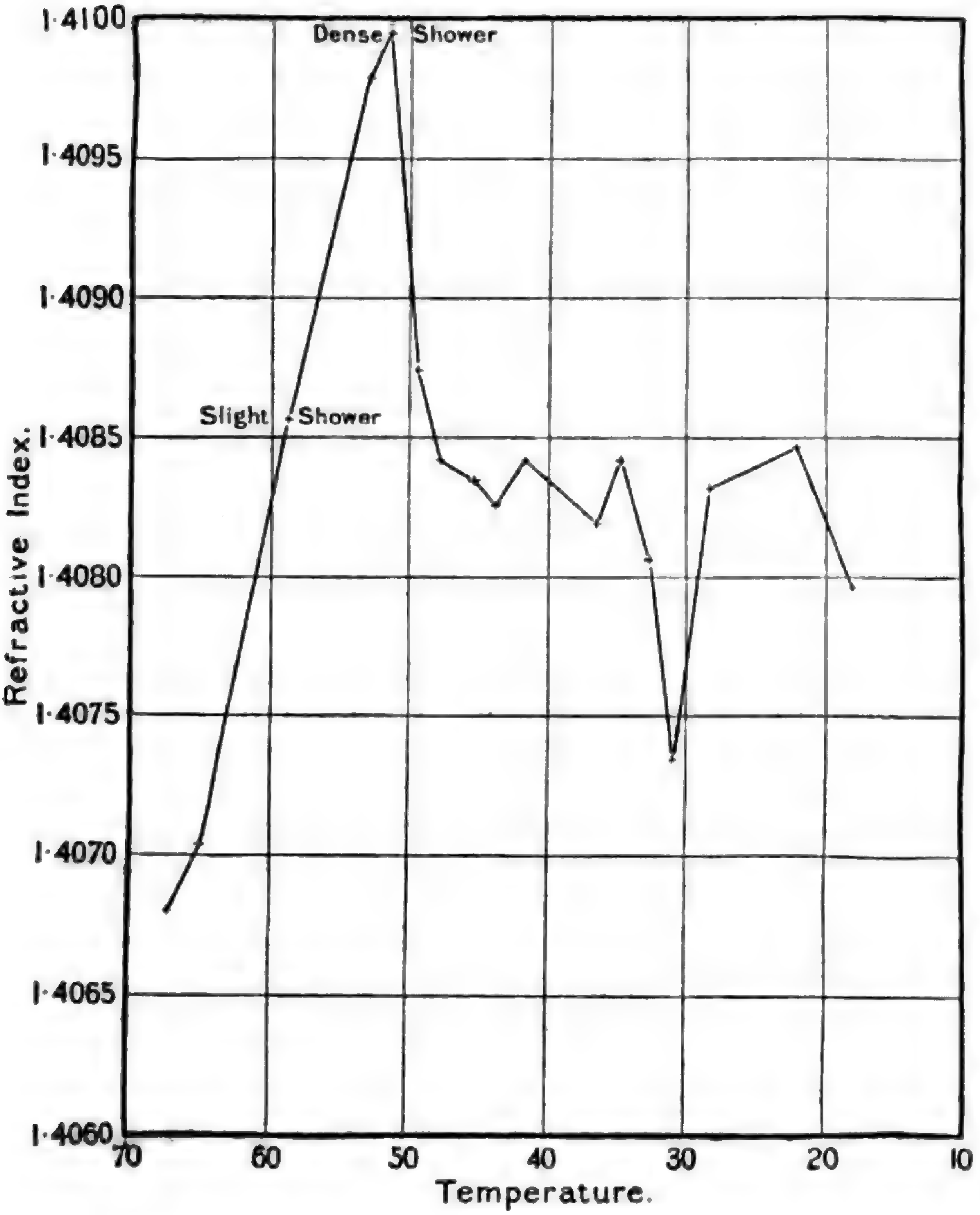
Expt. 1.—Composition: $NaNO_3 = 49{\cdot}505$, $Pb(NO_3)_2 = 11{\cdot}653$, $H_2O = 38{\cdot}842$ per cent. This solution was examined in the trough of the new goniometer. The trough was heated to 50° before introducing the solution, which was then covered with a layer of warm olive oil. The index rose from 1·405342 at 73·5° to 1·409956 at 51·4°, and fell from this value to 1·408258 at 43·8°; it then oscillated, rising and falling slightly as the temperature fell steadily until it reached 1·40743 at 31°. From this value it rose again to 1·408462 at 22·2°, and then fell to 1·407954 at 18°. A slight shower of crystals occurred at 58°, and a dense shower at 51·4°.

The changes of index in this experiment are completely shown in Fig. 2.

Expt. 2.—Composition: $NaNO_3 = 49{\cdot}020$, $Pb(NO_3)_2 = 11{\cdot}765$, $H_2O = 39{\cdot}215$ per cent. This solution was examined in the trough of the new goniometer, the solution was covered with a layer of warm olive oil, and the temperature kept from falling too rapidly at first by passing warm water over the sides of the trough. The index rose from 1·404491 at 74° to 1·409989 at 51°, and fell from this value to 1·408632 at 46·5°. As the temperature fell still further, the index rose and fell in an oscillatory manner and finally reached 1·406902 at 18°. Crystals appeared at 56°, and a dense shower occurred at 51°. The solution was clear again at 46·5°, and another opaque shower occurred suddenly at 38°.

Expt. 3.—Composition : $NaNO_3 = 48·515$, $Pb(NO_3)_2 = 11·881$, $H_2O =$ 30·604 per cent. This solution was covered with a layer of warm olive oil, and was examined in the trough of the new goniometer, which was heated before introducing the solution. The index rose from 1·403740 at 73° to 1·409279 at 46°, and fell from this value to

FIG. 2.



1·406326 at 30·5°. It then rose again, reaching 1·407649 at 25°, and finally fell to 1·407346 at 17·5°. A fine shower occurred at 56° on the upward branch of the index-temperature curve, and became much denser at 49°. An opaque shower occurred at 36°.

Expt. 4.—Composition: $NaNO_3 = 48·013$, $Pb(NO_3)_2 = 12·006$, $H_2O = 39·981$ per cent. This solution was covered with warm oil. The index rose from 1·405171 at 65° to 1·410460 at 42·5° and then fell. Crystals appeared at 60°, and a dense shower occurred at 42·5°.

Expt. 5.—Composition: $NaNO_3 = 47·981$, $Pb(NO_3)_2 = 12·037$, $H_2O = 39·982$ per cent. The index rose from 1·408021 at 61° to 1·411268 at 43°, and then fell suddenly to 1·409242 at 41°. The index continued to fall as the temperature was lowered, but in an oscillatory manner; it rose a little at about 20° and then fell again. Crystals appeared at 65° and fell to the bottom immediately. A fine shower of sodium nitrate crystals appeared at 58°, and a dense shower at 42°, rendering the solution opaque.

Expt. 6.—Composition: $NaNO_3 = 47·995$, $Pb(NO_3)_2 = 12·009$, $H_2O = 39·996$ per cent. The index rose from 1·406496 at 63° to 1·410562 at 40·5°, and fell from this value to 1·408326 at 32°. The index then rose from this to 1·408735 at 26°, after which it began to fall again at lower temperatures. Crystals appeared floating on the surface at 63°; a fine shower occurred at 49° on the upward branch of the refractive index-temperature curve, and a very dense shower fell at 40° after the maximum index was reached.

Expt. 7.—Composition: $NaNO_3 = 46·965$, $Pb(NO_3)_2 = 12·248$, $H_2O = 40·787$ per cent. This solution was covered with warm oil. The index rose from 1·403031 at 70° to 1·410766 at 38°. Crystals appeared at 45°, and a dense shower occurred at 36°.

Expt. 8.—Composition: $NaNO_3 = 46·950$, $Pb(NO_3)_2 = 12·244$, $H_2O = 40·806$ per cent. The index rose from 1·406598 at 56·5° to 1·410460 at 37°. It fell rather suddenly from this value to 1·408735 at 33°, and continued to fall much more slowly until the temperature reached 25°. The index then remained constant for some time, after which it began to rise slowly. Crystals appeared at 56°, and a fine shower occurred at 44° on the upward branch of the index-temperature curve. A dense shower occurred at 35°.

Expt. 9.—Composition: $NaNO_3 = 46·940$, $Pb(NO_3)_2 = 12·263$, $H_2O = 40·797$ per cent. The index rose from 1·406090 at 58° to 1·410310 at 39°. It then fell suddenly from this value to 1·408275 at 36°. The index then remained approximately constant until the temperature reached 26°, where the index was 1·408126. Crystals appeared at 58°, and a fine shower occurred at 49°. This fine shower continued until the temperature was 39°, when a much thicker shower fell rapidly, rendering the solution opaque.

Expt. 10.—Composition: $NaNO_3$ = 47·147, $Pb(NO_3)_2$ = 12·198, H_2O = 40·655 per cent. The index rose from 1·404967 at 64° to 1·410460 at 40°. It then fell gradually to 1·409346 at 34°, and then more suddenly to 1·408022 at 33°. After this the index remained very approximately constant until the temperature fell to 17°. Crystals appeared at 60°, and a fine shower occurred at 41°. This shower continued until the temperature was 34°, when a dense shower of crystals caused the solution to become opaque.

Expt. 11.—Composition: $NaNO_3$ = 46·145, $Pb(NO_3)_2$ = 12·436, H_2O = 41·419 per cent. The index rose from 1·406394 at 56° to 1·410562 at 35°, and then fell suddenly to 1·408327 at 30°. The index remained constant at this value until the temperature fell to 20°, and then rose to 1·408530 at 14°. Crystals appeared at 54°, and a fine shower occurred at 47°. A dense shower fell at 32°.

Expt. 12.—Composition: $NaNO_3$ = 45·833, $Pb(NO_3)_2$ = 12·511, H_2O = 41·656 per cent. This solution was covered with warm oil. The index rose from 1·403337 at 64° to 1·410009 at 33°, and fell from this value to 1·408123 at 27°. The index then remained constant until the temperature reached 18°. Crystals appeared at 33°, and a dense shower of crystals fell at 32·8°. At 31·5° the solution was almost clear again.

Expt. 13.—Composition: $NaNO_3$ = 45·149, $Pb(NO_3)_2$ = 12·706, H_2O = 42·145 per cent. The index of this solution rose from 1·403235 at 62° to 1·410212 at 32°, and then fell suddenly from this value to 1·407411 at 29°. It then fell very gradually to 1·407310 at 26°, and from this temperature it rose again to 1·408225 at 15°. Crystals appeared at 46°. A very fine shower occurred at 41°, and a very dense shower at 30°, causing the solution to become quite opaque with a rise of temperature of 0·5°.

Expt. 14.—Composition: $NaNO_3$ = 44·900, $Pb(NO_3)_2$ = 12·712, H_2O = 42·388 per cent. This solution was covered with a layer of warm oil. The index rose from 1·403133 at 61° to 1·410511 at 29°, and then fell from this value to 1·407615 at 22°. The solution was not cooled below 22°. Crystals appeared at 38°, and a dense shower occurred at 25°.

Expt. 15.—Composition: $NaNO_3$ = 44·484, $Pb(NO_3)_2$ = 12·811, H_2O = 42·705 per cent. This mixture was examined in the trough of the new goniometer. The trough was heated to 50° before introducing the solution, which was then covered with a layer of warm olive oil. The index rose from 1·401403 at 66·7° to 1·410227 at 30°, and fell from this value to 1·408021 at 21·5°. A shower of crystals occurred at 30°.

Expt. 16.—Composition: $NaNO_3$ = 44·460, $Pb(NO_3)_2$ = 12·822, H_2O = 42·718 per cent. The index rose from 1·402725 at 64° to

1·410562 at 31·5°, and then fell from this value to 1·408225 at 22°. The index then remained constant until the temperature reached 18°. Crystals appeared at 45°, and a dense shower occurred suddenly at 31°.

Expt. 17.—Composition: $NaNO_3 = 43·630$, $Pb(NO_3)_2 = 13·021$, $H_2O = 43·349$ per cent. The index rose from 1·401507 at 60° to 1·409142 at 27°. It then fell suddenly from this value to 1·407513 at 26°. The index afterwards rose slightly and then fell again very gradually. Crystals first appeared at 38°, a very fine shower occurred at 35°, and a dense shower at 26°, causing the temperature to rise 0·3°.

Expt. 18.—Composition: $NaNO_3 = 43·479$, $Pb(NO_3)_2 = 13·055$, $H_2O = 43·466$ per cent. This solution was covered with a layer of warm oil. The index rose from 1·401201 at 61° to 1·409754 at 25°, and then fell suddenly to 1·408123 at 24·5°. It then rose slowly, reaching 1·408429 at 17°. Crystals first appeared at 31°, and a dense shower occurred at 24·5°, causing the temperature to rise 0·3°.

Expt. 19.—Composition: $NaNO_3 = 43·470$, $Pb(NO_3)_2 = 13·052$, $H_2O = 43·478$ per cent. The index rose from 1·401608 at 63° to 1·410460 at 26°, and fell from this value to 1·408022 at 19·5°. It then rose again to 1·408430 at 17°. Crystals appeared at 35°, and a dense shower fell at 25°, causing the solution to rise 1° in temperature.

Expt. 20.—Composition: $NaNO_3 = 42·601$, $Pb(NO_3)_2 = 13·253$, $H_2O = 44·146$ per cent. The index rose from 1·401405 at 59° to 1·409855 at 24°, and fell from this value to 1·408123 at 21·8°. Crystals first appeared floating on the surface at 33°, and a shower of crystals occurred at 23·5°, fine at first, but becoming opaque after five minutes.

Expt. 21.—Composition: $NaNO_3 = 42·238$, $Pb(NO_3)_2 = 13·347$, $H_2O = 44·415$ per cent. The index rose from 1·399147 at 65° to 1·409550 at 20·5°, and fell from this value to 1·406800 at 12°. This mixture was covered with a layer of warm oil. A minute crystal appeared at 23°. A shower occurred at 19·4° which became somewhat dense in time. At 19·2° the solution was clear.

Expt. 22.—Composition: $NaNO_3 = 42·211$, $Pb(NO_3)_2 = 13·373$, $H_2O = 44·416$ per cent. The index rose from 1·401811 at 54° to 1·409042 at 23°, and fell from this value to 1·408378 at 19·25°. The index then remained approximately constant until the temperature reached 15°. Crystals first appeared at 30°. A fine shower occurred at 25°, and a dense shower at 20°.

Experiments with Sealed Tubes.

An attempt was made to verify the supersolubility curve *T* obtained from the refractive indices by the independent method which was employed with simple solutions.

Solutions containing sodium nitrate, lead nitrate, and water were enclosed in sealed test-tubes. The proportion of lead nitrate to water was 3 : 10, whilst the amount of sodium nitrate varied from 43·18 to 49 81 parts to 100 parts of solution.

The tubes were immersed in boiling water and shaken vigorously by hand from time to time until all the crystals were dissolved; they were then laid in a horizontal position on a rocker immersed in a hot-water bath, and shaken backwards and forwards on it by means of an electric motor.

The temperature at which crystals appeared in the tubes may be the temperature of spontaneous crystallisation or some lower temperature.

These solutions did not, on the whole, give such consistent results as did the simple solutions, as will be seen from the following experiments:

Expt. 23.—Composition: $Pb(NO_3)_2 = 12·875$, $NaNO_3 = 43·182$, $H_2O = 43·943$ per cent. This tube was boiled in water to dissolve all the crystals, and then shaken in the water-bath. It was cooled to 13° without formation of crystals. It will be seen from Fig. 1, obtained from the refractive indices of the solutions, that the solution in this tube should have crystallised spontaneously at 23°. The solution was somewhat viscous. The next morning a large sodium nitrate crystal had appeared in the tube, the temperature of which had not fallen below 12°.

Expt. 24.—Composition: $Pb(NO_3)_2 = 12·975$, $NaNO_3 = 43·777$, $H_2O = 43·248$ per cent. This tube should have crystallised at 25° according to Fig. 1. It was boiled for eighteen hours to dissolve the crystals, but when shaken in the hot-water bath the solution did not crystallise until the temperature reached 21°.

Expt. 25.—Composition: $Pb(NO_3)_2 = 12·777$, $NaNO_3 = 44·634$, $H_2O = 42·589$ per cent. From Fig. 1 the temperature of spontaneous crystallisation for this tube should be 29·2°. Crystals appeared in the tube at 29·5°. In this case the tube was boiled for one hour only to dissolve the crystals.

Expt. 26.—Composition: $Pb(NO_3)_2 = 12·944$, $NaNO_3 = 45·113$, $H_2O = 41·943$ per cent. From Fig. 1 the temperature of spontaneous crystallisation for this tube is 31·5°. The tube was boiled for one hour to dissolve the crystals, and, when cooled in the water-bath, it yielded crystals in a shower at 31°. When this tube was heated in boiling water for eighteen hours, the shower of crystals did not occur until the temperature fell to 29°. The solution also crystallised at 28·5°, after being heated in boiling water for a whole night.

Expt. 27.—Composition: $Pb(NO_3)_2 = 12{\cdot}454$, $NaNO_3 = 46{\cdot}030$, $H_2O = 41{\cdot}516$ per cent. From Fig. 1 the temperature of spontaneous crystallisation for this solution is 35°. When the tube was boiled in water for one hour, and then cooled in a hot-water bath and shaken continually, crystals first appeared at 34·8°. When, however, the tube was left in boiling water for a whole night and then cooled, spontaneous crystallisation did not occur until 29°.

Expt. 28.—Composition: $Pb(NO_3)_2 = 12{\cdot}50$, $NaNO_3 = 47{\cdot}28$, $H_2O = 40{\cdot}22$ per cent. From Fig. 1 the temperature of spontaneous crystallisation for this solution is 41·5°. The tube was boiled for one hour, and then shaken continually while cooling in the water-bath. Crystals appeared in a shower at 41°.

Expt. 29.—Composition: $Pb(NO_3)_2 = 11{\cdot}811$, $NaNO_3 = 48{\cdot}820$, $H_2O = 39{\cdot}369$ per cent. From Fig. 1 the temperature of spontaneous crystallisation for this solution is 50·5°. When the tube was boiled in water for a few hours, then cooled in a hot-water bath and shaken continually by hand, crystals first appeared at 51°. When the tube was boiled for a whole night, spontaneous crystallisation did not occur until 49·5°. This tube contained angular fragments of glass.

Expt. 30.—Composition: $Pb(NO_3)_2 = 11{\cdot}642$, $NaNO_3 = 49{\cdot}552$, $H_2O = 38{\cdot}806$ per cent. From Fig. 1 the temperature of spontaneous crystallisation for this solution is 54·5°. When the tube was boiled for a few hours and then allowed to cool in a water-bath while it was rocked by means of an electric motor, crystals first appeared at 54°. When boiled for a longer period, crystals did not appear until 51·5°. This tube also contained angular glass fragments.

Expt. 31.—Composition: $Pb(NO_3)_2 = 11{\cdot}583$, $NaNO_3 = 49{\cdot}810$, $H_2O = 38{\cdot}607$ per cent. This tube was boiled for several hours and then shaken continually while it was allowed to cool in a hot-water bath. Crystals appeared spontaneously at 56·5°. None of the experiments in the open trough has been made with solutions containing so large a quantity of sodium nitrate, but it will be seen from Fig. 1 that this experiment gives a point on the continuation of the supersolubility curve already obtained. This tube also contained angular glass fragments.

It appears from these experiments that the solutions crystallise very approximately on the supersolubility curve as determined from the refractive index provided they are not boiled for more than a few hours before they are allowed to cool. The crystals in all the tubes appeared to be completely dissolved in this time, and the tubes were always shaken vigorously by hand to aid the process. If, however, the tubes were boiled for a longer period, such as from eighteen to thirty hours, the solutions did not crystallise at temperatures corresponding with the supersolubility curve. Mere shaking was not enough to cause them to crystallise, and they passed into the labile state and became very viscous before the shower of crystals appeared. The tubes containing the larger amounts of sodium nitrate crystallise spontaneously at temperatures which show that the supersolubility curve changes its direction above 40° and bends towards the solubility curve. This agrees with the experiments on the refractive indices of the solutions. It was noticed that in the tubes of this set containing the larger amounts of sodium nitrate, the crystals which first made their appearance were very few and grew slowly. After the temperature had fallen considerably, however, an opaque shower of crystals appeared in the tubes. This behaviour appears to correspond with the second opaque showers already observed in the experiments on the refractive indices of some of the stronger solutions made in the trough of the goniometer.

The Effect of Rapid Cooling.

Expt. 32.—By means of the new goniometer, it was possible to investigate the effect of rapidly cooling the solutions. Cold water was passed over the sides of the trough containing the warm solution, while the changes in its index were watched.

A solution of sodium nitrate in a 3 : 10 solution of lead nitrate and water was heated and poured into the trough at about 70°. The composition of the solution was $NaNO_3 = 45{\cdot}833$, $Pb(NO_3)_2 = 12{\cdot}500$, $H_2O = 41{\cdot}666$ per cent. It was covered with a layer of warm oil, and then rapidly cooled and stirred continually.

The index rose from 1·401808 at 70° to 1·411268 at 24·5°, and then fell from this value to 1·406969 at 13·8°. Crystals appeared in the trough at about 40°, and a shower took place at 24·5°. A further opaque shower of crystals occurred at 20·5°, raising the temperature to 21°.

The solution cooled from 70° to 20° in seventeen minutes, and from 20° to 13·8° in twenty-six minutes.

If the solution had been allowed to cool gradually under the same conditions, crystals would probably have first appeared in the trough at about 43°, the temperature of saturation, and the index would have reached a maximum of about 1·410 at 33°, and then have decreased again as in experiment 12, in which the solution had approximately the same constitution. The rapid cooling therefore causes the solution to pass into the labile state, as may be seen from Fig. 1.

Expt. 33.—In a second experiment, the solution was also cooled rapidly in the same manner.

The composition of the solution was $NaNO_3 = 43·478$, $Pb(NO_3)_2 = 13·044$, $H_2O = 43·478$ per cent., the proportion of lead nitrate to water being 3 : 10, as before. The solution was poured into the trough at about 70° and immediately covered with a layer of warm oil. It was then cooled rapidly by passing cold water over the sides of the trough. The index rose from 1·401709 at 61° to 1·411302 at 17·5°, and then fell from this value to 1·408055 at 14·2°. The cooling was effected in about half an hour. Crystals first appeared at 35°, and a slight shower of crystals occurred at 17·5°. At 15° an opaque shower occurred, causing the temperature to rise to 15·5°. If allowed to cool gradually, crystals would probably have appeared in this solution at about 31°, and the index would have reached a maximum of about 1·4097 at 25°. In this experiment also, therefore, the rapid cooling causes the solution to pass far into the labile state, and to give a maximum index distinctly greater than that which would have been attained had the solution been cooled gradually.

The Effect of Prolonged Heating.

Expts. 34 and 35.—In the following experiments the solutions were heated and placed in the goniometer trough, which had been previously heated to about 50° by passing hot water over the sides of the trough. The solution was immediately covered with a layer of warm olive oil, and hot water was continually passed over the sides of the trough to delay the rate of cooling. The composition of the solution treated in this manner was $NaNO_3 = 43·478$, $Pb(NO_3)_2 = 13·044$, $H_2O = 43·478$ per cent., the proportion of water to lead nitrate being 10:3, as in the preceding experiments.

The solution was placed in the trough at 70° and cooled gradually, the temperature of the hot water passing over the sides of the trough being about 50°.

The index rose from 1·399844 at 70° to 1·404610 at 50°, somewhat rapidly at first and then very slowly. It remained approximately constant at this temperature for three-quarters of an hour, no crystals appearing in the trough during this time. Comparison with Fig. 1 shows the solution to be unsaturated at this temperature. The temperature of the water passing over the sides of the trough was then lowered to about 30°, when the index began to rise again from 1·404610 at 50° to 1·409262 at 28·2°, and remained very approximately constant at this temperature for three-quarters of an hour. It may be seen from the diagram that the solution is now in the metastable state. Crystals appeared in the trough at 33° just after the solubility curve *S* was crossed. The stream of water over the sides of the trough was then stopped, and the solution was allowed to cool naturally, the index rising from 1·409262 at 28·2° to 1·409873 at 24°, where it just touched the supersolubility curve, and then falling from this value to 1·408309 at 21°. An opaque shower of crystals occurred in the trough at 22°. Therefore, beyond causing slight irregularities in the index-temperature curve at 50° and 28·2°, the prolonged heating of the solution at these temperatures produces no effect, and the results of this experiment, if plotted on Fig. 1, will not differ from any of the preceding experiments in general character.

In another experiment the temperature of the solution was again kept from falling for a considerable time, but the general result was the same as before, the index rising, with slight irregularities, until the supersolubility curve was reached, and then falling again.

Effect of introducing a Mass of Crystals into a just saturated Solution.

Expt. 36.—In the following experiment a solution containing 45 per cent. of sodium nitrate and 55 per cent. of a 3 : 10 lead nitrate solution in water was heated to 70°, placed in the warm trough of the goniometer, and immediately covered with a layer of warm olive oil. It was stirred vigorously. This solution is just saturated with respect to sodium nitrate at about 41·5°, and its index was observed to rise from 1·402231 at 68° to 1·408513 at 41°, no crystals having yet appeared in the trough. At 40° a quantity of sodium nitrate crystals warmed to 40° was suddenly introduced into the saturated solution, bringing the percentage of sodium nitrate up to 49. The introduction of these crystals caused a dense shower to appear in the solution, but no appreciable change of temperature. The index, however, began to fall at once from 1·408513 at 41° to 1·408105 at 40°; it then rose again, reaching 1·408987 at 34°. A second fine shower occurred at 34°, and the index fell again, reaching 1·407766 at 29°, and then rose until it reached 1·408547 at 18°. Had the original solution containing 45 per cent. of sodium nitrate been stirred and allowed to cool gradually without introducing the excess of sodium nitrate crystals, the index would have risen steadily to about 1·4102 at 31·5°, the labile temperature. The introduction of the crystals, however, appears to relieve the supersaturation at once and prevent the solution from ever reaching the supersolubility curve. The solution remains in the metastable region as the temperature falls, and finally oscillates about the solubility curve, as in some of the preceding experiments. In fact, after the introduction of the extra crystals, bringing the percentage of sodium nitrate up to 49, the solution behaves as if it had always contained this amount and had reached the supersolubility curve at some higher temperature, the concentration of the solution falling immediately the excess of crystals was introduced.

Solubility Curve.

Fig. 1 also contains the solubility curve *S*, which shows the percentage of sodium nitrate in a saturated solution of lead nitrate and water (in the proportion of 3 : 10) at different temperatures.

The solubility curve *S* was determined by the method used and described by Hartley (Trans., 1906, **89**, 1015).

Weighed quantities of sodium nitrate and lead nitrate solution were enclosed in sealed tubes of Jena glass. They were then heated in a water-bath until all the crystals had dissolved with the exception of one or two very small sodium nitrate crystals, which were preserved at the upper end of the tube. The tubes containing these crystals were then shaken continually and watched as they cooled in a beaker of water. The small crystals appeared to dissolve at first, and their edges became rounded until the water-bath fell to a certain temperature, after which the crystals were seen to grow, their edges becoming quite sharp. This change is quite distinct, and the temperature at which it occurs is taken as the temperature of saturation.

In experiments 37, 38, 39, 40, 48, 49, 50, 51 and 52, the tubes were not sealed, but were firmly closed with a rubber stopper. In these tubes the crystals were dissolved by boiling, and the solutions were then inoculated with a minute crystal of sodium nitrate. This crystal at first begins to dissolve in the warm solution, but when the temperature has fallen to a certain point it begins to grow again, and forms a slight metastable shower around itself. This temperature is taken to be the temperature of saturation. Each experiment was repeated once or twice, and the results obtained never varied more than about 0·5°. The mean of the values was taken as the true temperature of saturation.

The following are the results obtained :

	Percentage composition of the solution.			
Experiment.	$NaNO_3$.	$Pb(NO_3)_2$.	H_2O.	Temperature of saturation for NaNO .
37	40·97	13·622	45·408	21°
38	41·5	13·5	45·0	24
39	42·037	13·376	44·587	26·5
40	42·500	13·269	44·231	28·5
41	43·182	12·875	43·943	31
42	44·605	12·751	42·644	37·8
43	44·634	12·777	42·589	38·8
44	45·113	12·944	41·943	41
45	45·700	12·407	41·893	43
46	46·030	12·454	41·516	44·25
47	47·28	12·50	40·22	51
48	48·020	11·994	39·986	56
49	48·426	11·902	39·672	56·5
50	49·025	11·763	39·212	58
51	49·502	11·653	38·845	61
52	49·923	11·556	38·521	64

These results when plotted on Fig. 1 are seen to lie very approximately on a straight line *S*, the solubility curve for sodium nitrate in a 30 per cent. solution of lead nitrate and water. The line *S* is inclined at a small angle to the supersolubility curve *T*, and is separated from it by an interval of about 7° of temperature at the upper end, 9·5° of temperature at the centre, and 4·5° of temperature at the lower end of the diagram.

It is to be noted that throughout the whole of this series of experiments the crystals separating from the solutions as they cooled were examined from time to time under the microscope, and in every case they were found to be ordinary rhombohedra of sodium nitrate.

FIG. 3.

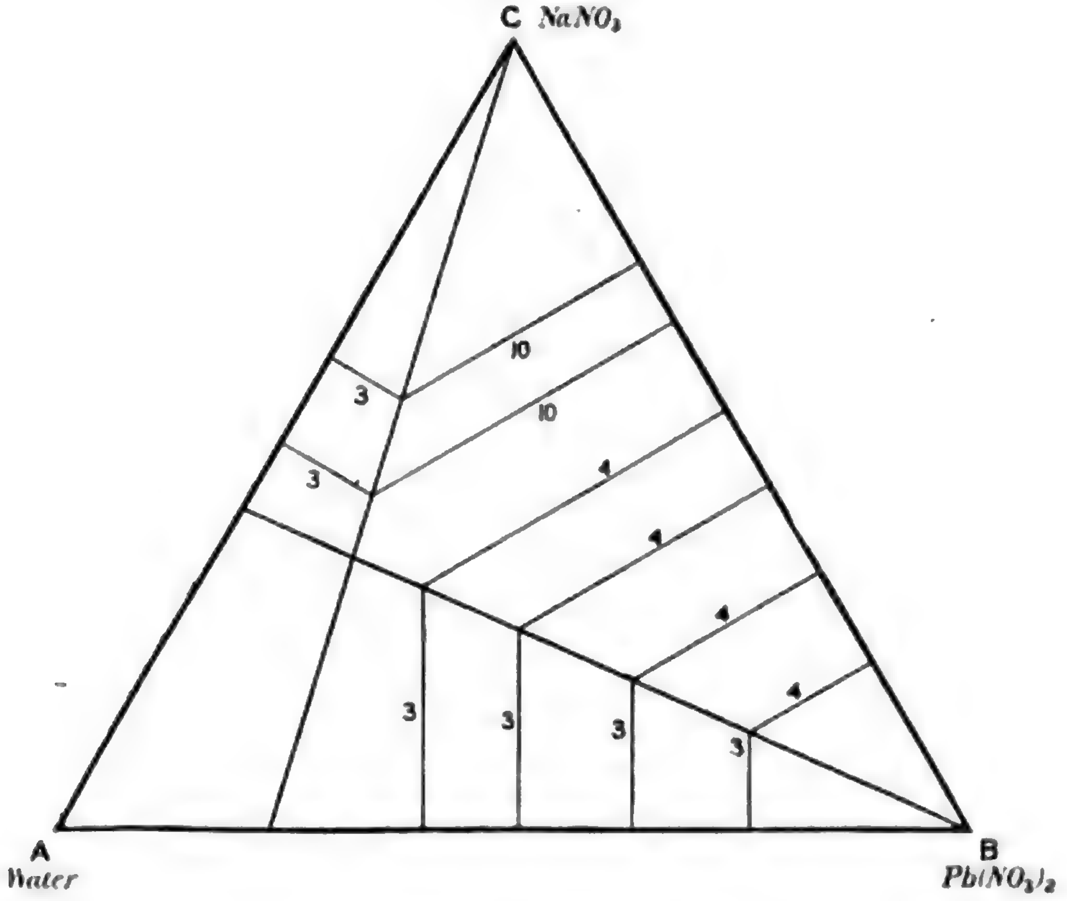


Fig. 1 may be regarded as a section of the surface which gives the temperatures of solidification of all mixtures of the three substances water, sodium nitrate, and lead nitrate. This is a solid figure having an equilateral triangle *ABC* as base (Fig. 3), in which the concentration at any point of the solid figure is given by the projections of the perpendicular distances of the point from the sides of the triangle, the temperature being measured perpendicular to the plane of the paper. The corners *A*, *B*, *C*, of the triangle represent the substances water, lead nitrate, and sodium nitrate respectively. Since in the above experiments the ratio of the quantity of lead nitrate to water was kept constant for all the solutions examined, Fig. 1 represents a section of the surface by a plane passing through the edge C of the right prism of which ABC is the base, in a direction given by the ratio 3 : 10, and perpendicular to the plane of the paper.

Second Set of Experiments.—Solutions containing Excess of Lead Nitrate.

In the second set of experiments, the proportion of sodium nitrate to water was kept constant and the amount of lead nitrate varied in the different solutions. Throughout this set of seventeen experiments, the proportion of sodium nitrate to water was very approximately as 75 : 100, whilst the amount of lead nitrate varied from 24·893 to 19·739, the whole solution being taken as 100. As in the first set of experiments, the solutions were placed in the goniometer trough at about 60°, and their refractive indices were observed as they cooled to about 15°.

Throughout this set of experiments, octahedra of lead nitrate crystallised out of the solutions as they cooled, but no sodium nitrate separated.

Fig. 4 gives the results of all the experiments of this set. In nine of these experiments, the solutions were introduced into the trough at a high temperature and immediately covered with a layer of hot olive oil. This prevented any evaporation from the surface of the trough, and until crystals began to form in the solution the concentration was consequently constant.

From the results of five of these experiments with oil-covered solutions, curves of constant refractive index were plotted on a concentration-temperature diagram. These curves were drawn for the following values of refractive index: 1·405, 1·406, 1·407, 1·408, 1·409, 1·410, 1·411, 1·412, 1·413, and are shown on the diagram. They were found to be very approximately straight lines parallel to each other and equidistant, inclined at an angle of 52° 59′ to the temperature axis, the scale being such that 1 per cent. of lead nitrate corresponds with 10° of temperature.

If a line be drawn perpendicular to these constant index curves, it will be possible as before to measure along this line the refractive index of any solution as it cools.

The curves on Fig. 4, showing the behaviour of the various solutions, are all plotted from the observed values of their refractive indices as they cooled, in the manner indicated above.

In the remaining eight experiments of this set, the solutions were not covered with a layer of olive oil as soon as they were introduced into the trough, so that evaporation from the surface of the liquid caused a slight increase in the concentration of the solutions through-

refractive indices rise steadily with fall of temperature. There are sometimes slight irregularities in the curves where they cross the solubility curve S. Here crystals usually make their appearance, after which the concentration generally drops slightly for the various solutions. The refractive indices, however, continue to rise until they reach a maximum, and then fall again, slowly at first and then very rapidly until the curves finally touch the solubility curve S. Shortly after the maximum index is reached, a dense shower of crystals takes place throughout the solution, causing the rapid fall in the index and concentration. The diagram shows that at the points where the solutions reach their maximum indices all the curves approximately touch a continuous curve T. This curve T is almost a straight line parallel to the solubility curve S for temperatures varying from 20° to 40°. Above 40°, however, the curve bends towards the solubility curve S, and indicates that the metastable region for the stronger solutions examined is considerably narrower than the metastable area for the weaker solutions. This curve T is the supersolubility curve for the set of mixtures containing from 24·893 to 19·739 per cent. of lead nitrate in a solution of sodium nitrate and water, the proportion of sodium nitrate to water being 3 : 4, and divides the metastable from the labile region.

Behaviour of Mixed Solutions of this Set compared with Simple Solutions.

The behaviour of the majority of the solutions of this set does not differ from that of the simple solutions in any essential details. In solutions containing less than 24·242 per cent. of lead nitrate, the refractive index rises to a maximum as the temperature falls, and then falls suddenly. Crystals appeared on the upward branch of the index-temperature curve, usually causing a very slight irregularity in the curve. The index continues to rise to a maximum and then falls very suddenly, a dense shower of crystals taking place during the fall in index. The rest of the solutions of this set, containing from 24·242 to 24·893 per cent. of lead nitrate, behaved in the same way except that after the index had risen to a maximum there was no sudden shower of crystals, but crystals grew rapidly at the bottom of the trough and the concentration streams rising from them were very marked.

The solutions of this set, however, differ from those of the previous one in that (i) there is no fine shower while the index is rising in the metastable region, as was the case with some of the solutions of that set; and (ii) the fall in index after the maximum index is reached is very sudden, but does not then become oscillatory as in some of the solutions of the first set.

The following are the results for the set of experiments described above :

Expt. 53.—Composition: $H_2O = 45{\cdot}856$, $NaNO_3 = 34{\cdot}405$, $Pb(NO_3)_2 = 19{\cdot}739$ per cent. The index rose from 1·405274 at 49° to 1·411880 at 20°, and then fell rapidly to 1·408530 at 19°. Crystals appeared at 30°, and a shower of crystals occurred at 20°.

Expt. 54.—Composition: $H_2O = 45{\cdot}444$, $NaNO_3 = 34{\cdot}101$, $Pb(NO_3)_2 = 20{\cdot}455$ per cent. This solution was covered with warm oil. The index rose from 1·403133 at 60° to 1·411472 at 23·8°, and fell from this value to 1·410663 at 21·7°. Crystals first appeared at 28°.

Expt. 55.—Composition: $H_2O = 45{\cdot}450$, $NaNO_3 = 34{\cdot}089$, $Pb(NO_3)_2 = 20{\cdot}461$ per cent. The index rose from 1·406296 at 48° to 1·411471 at 25°, and then fell from this value to 1·409652 at 22·5°. Crystals first appeared at 33°, and a fine shower occurred at 22·5°.

Expt. 56.—Composition: $H_2O = 45{\cdot}439$, $NaNO_3 = 34{\cdot}091$, $Pb(NO_3)_2 = 20{\cdot}470$ per cent. The index rose from 1·406090 at 50° to 1·412591 at 22·5°, and then fell from this value to 1·407613 at 18°. Crystals appeared at 32°, and a shower of crystals occurred at 22·5° which became very dense at 21·5°.

Expt. 57.—Composition: $H_2O = 44{\cdot}940$, $NaNO_3 = 33{\cdot}722$, $Pb(NO_3)_2 = 21{\cdot}338$ per cent. This solution was covered with a layer of warm oil. The index rose from 1·405477 at 57° to 1·412591 at 25°, and then fell from this value to 1·410967 at 21·6°. Crystals first appeared at 34·5°. The stirring was stopped as soon as the temperature had fallen to 25°.

Expt. 58.—Composition: $H_2O = 44{\cdot}934$, $NaNO_3 = 33{\cdot}703$, $Pb(NO_3)_2 = 21{\cdot}363$ per cent. The index rose from 1·405376 at 60° to 1·412389 at 31°, and then fell from this value to 1·407817 at 24°. Crystals appeared at 40°, and a shower of crystals occurred at 30·5°.

Expt. 59.—Composition: $H_2O = 44{\cdot}714$, $NaNO_3 = 33{\cdot}594$, $Pb(NO_3)_2 = 21{\cdot}692$ per cent. The index rose from 1·405783 at 59° to 1·413095 at 29°, and then fell from this value to 1·408225 at 23°. Crystals first appeared at 45·5°, and a slight shower occurred at 28° which became dense at 27°.

Expt. 60.—Composition: $H_2O = 44{\cdot}634$, $NaNO_3 = 33{\cdot}493$, $Pb(NO_3)_2 = 21{\cdot}872$ per cent. This solution was covered with a layer of warm oil. The index rose from 1·404865 at 61° to 1·412895 at 28°, and then fell from this value to 1·410663 at 25°. Crystals first appeared at 38° which grew rapidly at 29°, but no shower occurred in the solution.

Expt. 61.—Composition: $H_2O = 44{\cdot}447$, $NaNO_3 = 33{\cdot}352$, $Pb(NO_3)_2 = 22{\cdot}201$ per cent. The index rose from 1·407411 at 57·5° to 1·413905 at 31°, and then fell from this value to 1·408021 at 23°. Crystals first appeared at 40°. A slight shower of crystals occurred at 29° which became dense at 27°.

Expt. 62.—Composition: H_2O = 43·951, $NaNO_3$ = 32·967, $Pb(NO_3)_2$ = 23·083 per cent. The index rose from 1·408072 at 58° to 1·414107 at 33°, and then fell from this value to 1·407411 at 23·5°. Crystals first appeared floating at 55°, and at the bottom of the trough at 49·5°. A slight shower occurred at 29° which became dense at lower temperatures.

Expt. 63.—Composition: H_2O = 43·942, $NaNO_3$ = 32·975, $Pb(NO_3)_2$ = 23·083 per cent. This solution was covered with warm oil. The index rose from 1·407920 at 58° to 1·412844 at 36°, and fell from this value to 1·412287 at 33°. Crystals appeared at 47°.

Expt. 64.—Composition: H_2O = 43·475, $NaNO_3$ = 32·611, $Pb(NO_3)_2$ = 23·914 per cent. The index rose from 1·410460 at 56° to 1·414005 at 38·5°, and then fell from this value to 1·407513 at 23°. Crystals appeared at 56°, and a dense cloud of crystals occurred at 37·5°.

Expt. 65.—Composition: H_2O = 43·459, $NaNO_3$ = 32·616, $Pb(NO_3)_2$ = 23·925 per cent. This solution was covered with a layer of warm oil. The index rose from 1·407816 at 63° to 1·413602 at 38°, and then fell from this value to 1·408836 at 29°. Crystals first appeared at 50°.

Expt. 66.—Composition: H_2O = 43·196, $NaNO_3$ = 32 398, $Pb(NO_3)_2$ = 24·406 per cent. This solution was examined by the new inverted goniometer, the trough of which contains a much larger quantity of solution than that used in the previous experiments. The trough was warmed to about 50° before introducing the solution, which was immediately covered with a layer of warm olive oil. The index rose from 1·409584 at 62° to 1·412995 at 44°, and then fell from this value to 1·407581 at 21°. Crystals first appeared at 54°. No shower of crystals was seen, but after the highest index was reached the concentration streams were very marked and were seen rising from the bottom of the trough.

Expt. 67.—Composition: H_2O = 43·011, $NaNO_3$ = 32·258, $Pb(NO_3)_2$ = 24·731 per cent. This solution was also examined in the trough of the new goniometer. The trough was heated to 40° before introducing the solution, which was then covered with a layer of olive oil. The index rose from 1·409279 at 62·5° to 1·413197 at 43°, and then fell from this value to 1·407311 at 19°. Crystals appeared at 52°. An extremely slight shower of very small crystals occurred at 40°, and, as in the previous experiment, the concentration streams were very marked after the highest index was reached.

Expt. 68.—Composition: H_2O = 43·103, $NaNO_3$ = 32·328, $Pb(NO_3)_2$ = 24·569 per cent. This solution was examined in the trough of the new goniometer, which was heated to 40° before introducing the solution. The solution was covered with a layer of warm olive oil. The index rose from 1·406733 at 73° to 1·412927 at 46°, and fell from this value to 1·408258 at 20·5°. Crystals appeared at 58°, and an extremely slight shower of very small crystals occurred at 45°. The concentration streams were very marked in this experiment also.

Expt. 69.—Composition: H_2O = 42·919, $NaNO_3$ = 32·188, $Pb(NO_3)_2$ = 24·893 per cent. The solution was examined in the trough of the new goniometer. The trough was heated to 45° before introducing the solution, which was immediately covered with a layer of warm olive oil. The index rose from 1·408936 at 64° to 1·412254 at 47°, and fell from this value to 1·407411 at 27°. Crystals appeared at 58°. No shower occurred in this experiment, but crystals grew rapidly at the bottom of the trough, and the concentration streams were very marked.

Experiments with Sealed Tubes.

The supersolubility curve determined by the refractive indices for this set of experiments was also checked by the method of sealed tubes as already described (p. 393).

The solutions containing lead nitrate, sodium nitrate and water were enclosed in sealed tubes, the proportion of sodium nitrate to water being always 3 : 4, whilst the amount of lead nitrate varied from 24·933 to 20·328 parts to 100 parts of solution for the different tubes.

The tubes were heated in hot water to dissolve the crystals; they were then allowed to cool gradually in a water-bath, and as they cooled they were either shaken by hand or rocked by means of an electric motor.

The temperature at which crystals appeared in the tubes was taken to be the temperature of spontaneous crystallisation.

The following results were obtained:

Expt. 70.—Composition: H_2O = 42·895, $NaNO_3$ = 32·172, $Pb(NO_3)_2$ = 24·933 per cent. This tube was heated to 90° for twenty-four hours, and, the crystals having completely dissolved, was shaken by hand as it cooled in a water-bath. Lead nitrate crystals appeared at 56°. The experiment was repeated after heating the tube again to 90° for thirty-six hours. On cooling again and shaking by hand, crystals appeared at 55°. This tube contained angular fragments of glass with the solution. The crystals which first appeared were few and very small, and a shower of crystals did not occur until a much lower temperature was reached.

Expt. 71.—Composition: H_2O = 42·926, $NaNO_3$ = 32·194, $Pb(NO_3)_2$ = 24·880 per cent. This tube was heated to 102° for two hours to dissolve the crystals, and then shaken by hand in a water-bath. Crystals first appeared at 55°, but were very few and small; a shower did not occur until a much lower temperature. This tube also contained angular fragments of glass with the solution.

Expt. 72.—Composition: $H_2O = 43{\cdot}128$, $NaNO_3 = 32{\cdot}346$, $Pb(NO_3)_2 = 24{\cdot}526$ per cent. This tube was heated to 102° for two hours and then shaken by hand in a water-bath. Crystals appeared in a slight shower at 47°. The experiment was repeated after heating again to 90° for thirty-six hours to dissolve the crystals, and on cooling a slight shower occurred at 49°. This tube also contained angular fragments of glass.

Expt. 73.—Composition: $H_2O = 43{\cdot}282$, $NaNO_3 = 32{\cdot}462$, $Pb(NO_3)_2 = 24{\cdot}256$ per cent. This tube was heated to 90° for twenty-four hours to dissolve the crystals, and shaken by hand in a water-bath. Crystals first appeared in a shower at 46°. The experiment was repeated, and the tube was heated again to 90° for thirty-six hours. The shower of crystals then appeared at 45°. This tube also contained angular fragments of glass.

Expt. 74.—Composition: $H_2O = 43{\cdot}290$, $NaNO_3 = 32{\cdot}468$, $Pb(NO_3)_2 = 24{\cdot}242$ per cent. This tube was heated to 102° for two hours to dissolve the crystals, and then shaken by hand in a water-bath. Crystals appeared in a slight shower at 44°. This tube also contained glass fragments.

Expt. 75.—Composition: $H_2O = 43{\cdot}469$, $NaNO_3 = 32{\cdot}601$, $Pb(NO_3)_2 = 23{\cdot}930$ per cent. This tube was heated to 75° for twenty-four hours, and shaken on the rocker as it cooled in a water-bath. Crystals appeared in a shower at 39°. When heated for four days and nights at 85°, no crystals appeared until the temperature had fallen to 27·5°. This tube did not contain angular glass fragments.

Expt. 76.—Composition: $H_2O = 43{\cdot}721$, $NaNO_3 = 32{\cdot}791$, $Pb(NO_3)_2 = 23{\cdot}488$ per cent. This tube was heated to 100° for two and a-half hours, and then shaken by hand in a water-bath. Crystals appeared in a shower at 37·5°. The tube contained angular fragments of glass.

Expt. 77.—Composition: $H_2O = 43{\cdot}917$, $NaNO_3 = 32{\cdot}938$, $Pb(NO_3)_2 = 23{\cdot}145$ per cent. This tube was heated for two hours to 100° to dissolve the crystals, and then shaken by hand as it cooled in a water-bath. Crystals appeared in a shower at 31°. This tube did not contain angular fragments of glass.

Expt. 78.—Composition: $H_2O = 44{\cdot}464$, $NaNO_3 = 33{\cdot}348$, $Pb(NO_3)_2 = 22{\cdot}188$ per cent. This tube was heated for twenty-four hours to about 75° or 80°, and shaken on the rocker as it cooled in a water-bath. Crystals appeared in a shower at 29°. The tube was heated again to 85° for four days and nights to dissolve the crystals, and when shaken in the cooling water-bath crystals appeared at 27·5° in a shower.

Expt. 79.—Composition: $H_2O = 44·942$, $NaNO_3 = 33·706$, $Pb(NO_3)_2 = 21·352$ per cent. This tube was heated to 85° for four days and nights, and then shaken on a rocker in a cooling water-bath. This solution becomes labile at 25°, but no shower occurred in the tube though it was cooled gradually to 15°. After the lapse of a day or two, a large lead nitrate crystal had formed in the tube, the temperature of which had not fallen below 12°. The experiment was repeated, and the tube heated to 100° for two hours to dissolve all solid material. The same result was obtained, the tube being cooled to the temperature of the room and shaken violently by hand without crystals appearing. This tube contained no angular glass fragments.

Expt. 80.—Composition: $H_2O = 45·527$, $NaNO_3 = 34·145$, $Pb(NO_3)_2 = 20·328$ per cent. This tube was heated for four days and nights to 85° to dissolve the crystals, and shaken on the rocker as it cooled. It was cooled to 15° without any crystals appearing, although the solution becomes labile at about 21°. A single large lead nitrate crystal appeared after the lapse of a few days. The tube was then heated again for two hours to 100°, but was again cooled gradually to 15° without crystals having made their appearance, although shaken violently by hand continually. This tube did not contain any glass fragments.

From these experiments it appears that the solutions in the sealed tubes crystallise at temperatures which coincide approximately with those given by the supersolubility curve as determined by the refractive indices. Internal friction by means of angular glass fragments appears to be necessary to bring down the crystals on the supersolubility curve, otherwise the solutions pass into the labile state without crystallising, as in experiments 79 and 80 above. This was also found to be the case with sodium chlorate, as mentioned in the previous paper on spontaneous crystallisation. Provided the tubes contain the glass fragments, the length of time during which the tubes are heated does not appear to have much effect on the temperature of spontaneous crystallisation. The contents of the tubes containing the larger amounts of lead nitrate are seen to crystallise spontaneously at temperatures which show that the supersolubility curve changes its direction somewhat above 40°, and bends towards the solubility curve. From Fig. 4 it is seen that this change in the direction of the supersolubility curve above 40° is also indicated by the experiments on the refractive indices.

The Effect of Rapid Cooling.

The effect of rapid cooling was also investigated for this series of solutions, the method being the same as that described on p. 395.

Expt. 81.—The concentration of the solution was $H_2O = 44{\cdot}052$, $NaNO_3 = 33{\cdot}040$, $Pb(NO_3)_2 = 22{\cdot}908$ per cent., the proportion of sodium nitrate to water being 3 : 4.

The solution was poured into the warm trough at about 70°, covered with a layer of warm olive oil, and cooled rapidly by passing cold water over the sides of the trough. The index rose from 1·406937 at 61° to 1·417443 at 16°, and then fell from this value to 1·411033 at 13°, the time taken being sixteen minutes to cool from 65° to 20°, and half an hour to fall from 20° to 13°. Crystals first appeared at 22·5°, and a fine shower occurred at 15°.

If allowed to cool gradually under the same conditions, crystals would probably have first appeared at about 49°, the temperature of saturation, and the index would have reached a maximum of about 1·4138 at 32·5°, and then have decreased again as in experiment 61, in which the solution had approximately the same constitution. The rapid cooling, therefore, causes the solution to pass far into the labile state. This curve is not shown on the diagram; on crossing the supersolubility curve it showed a distinct irregularity.

Expt. 82.—In a second experiment, the solution was again rapidly cooled in the same manner. The concentration of the solution was $H_2O = 44{\cdot}444$, $NaNO_3 = 33{\cdot}333$, $Pb(NO_3)_2 = 22{\cdot}222$ per cent., the proportion of sodium nitrate to water being 3 : 4, as before. The solution was poured into the warm trough at 70°, and immediately covered with a layer of warm olive oil. It was then cooled rapidly by passing cold water over the sides of the trough.

The index rose from 1·404797 at 65° to 1·415211 at 18°, and fell from this value to 1·406869 at 11·5°. Crystals first appeared in a fine shower at 20° which became dense at 18°. If allowed to cool gradually, crystals would probably have appeared in this solution at about 34°, the temperature of saturation, and the index would have reached a maximum of about 1·4133 at 28°. In this experiment also, therefore, the rapid cooling causes the solution to pass far into the labile state.

Solubility Curve.

The solubility curve *S* on Fig. 4 shows the percentage of lead nitrate in a saturated solution of sodium nitrate and water in the proportion of 3 : 4.

The curve was determined in the manner already described on p. 398.

In experiments 83, 84, 85, 86, 87, and 88, the tubes were sealed, while in experiments 89, 90, and 91, the tubes were closed firmly with a rubber stopper.

The compositions of the solutions contained in these tubes are given below.

In all cases the solutions were inoculated with a minute crystal of lead nitrate in the manner described on p. 398, and the growth of the immersed crystal gives the temperature of saturation.

The following results were obtained :

	Percentage composition of the solution.			
Experiment.	H_2O.	$NaNO_3$.	$Pb(NO_3)_2$.	Temperature of saturation of lead nitrate in the solution.
83	45·892	34·420	19·688	32°, 32°
84	45·527	34·145	20·328	35·5°
85	44·942	33·706	21·352	38·5°, 40·5°, 40·5°
86	44·464	33·348	22·138	43°, 44°, 44°
87	43·917	32·938	23·145	48·5°, 50°, 49°, 49°
88	43·469	32·601	23·930	54°, 55°, 55°
89	43·290	32·468	24·242	58°, 58°, 59°
90	43·103	32·328	24·569	62°, 62°
91	42·918	32·189	24·893	65°, 64°, 66°

These results when plotted on Fig. 4 give the continuous curve *S*, the solubility curve for lead nitrate in a 3 : 4 solution of sodium nitrate in water. This curve (except at the upper end) is separated from the supersolubility curve already determined by 15° or 16° of temperature.

As in the first series of experiments, the crystals separating from these solutions throughout the second set of experiments were examined from time to time under the microscope and found to be indistinguishable from ordinary lead nitrate.

Fig. 4 may also be regarded as a section of a surface having an equilateral triangle *ABC* as base (compare Fig. 3), in which the concentration at any point of the solid figure is given by the projection of the perpendicular distances of the point from the sides of the triangle. The temperature is measured perpendicular to the plane of the paper. As before, let the corners *A*, *B*, *C*, of the triangle represent the substances water, lead nitrate, and sodium nitrate. Since in the above experiments the ratio of the quantity of sodium nitrate to water was kept constant at 3 : 4 for all the solutions examined, Fig. 4 represents a section of the surface by a plane passing through the edge *B* of the right prism of which *ABC* is the base, in the direction given by the ratio 3 : 4, perpendicular to the plane of the paper.

General Conclusions.

The preceding experiments have established for a mixture of three constituents the principles of crystallisation previously established for binary mixtures (Trans., 1906, **89**, 413).

With the three constituents sodium nitrate, lead nitrate, and water, any mixture has a perfectly definite temperature of spontaneous crystallisation, that is, a temperature above which it cannot be made to crystallise except by inoculation. This is shown by the shower which forms in the solutions in the open trough, the maximum value attained by the refractive index, and the shower in the sealed tubes.

Solutions exposed to the air, and containing a large proportion of sodium nitrate, when stirred exhibit a slight metastable shower in the open trough before the temperature of spontaneous crystallisation is reached, but this shower is extremely slight, and easily distinguished from the very dense shower which occurs at the temperature of spontaneous crystallisation; the latter usually renders the solution opaque.

It must be observed that the solution in which the metastable shower occurs already contains growing crystals of sodium nitrate. In order to prove that this shower also consists of sodium nitrate, it was examined more minutely in an experiment made under the microscope. A solution in which the concentration of sodium nitrate was 46·94 per cent. in a 3 : 10 aqueous solution of lead nitrate was placed in a watch-glass at a high temperature and examined under the microscope as it cooled gradually. The solution was stirred with a pin point, and sodium nitrate crystals first appeared floating on the surface; then a slight shower corresponding to the metastable shower referred to in this paper, and finally, when the temperature had fallen sufficiently, the labile shower occurred in which crystals also formed on the watch-glass along the lines of scratch. Throughout the experiment, all the crystals had the appearance and optical properties of ordinary sodium nitrate.

The temperature of spontaneous crystallisation varies with the concentration of the solution, and for the two series of solutions examined these temperatures are found to lie on continuous curves; these have been termed the supersolubility curves. They may be regarded as plane sections in two directions of a surface which may be termed the supersolubility surface for every possible mixture of the three constituents sodium nitrate, lead nitrate, and water.

The same solutions enclosed in sealed glass tubes cannot be made to crystallise at a higher temperature than that given by the supersolubility curve except by inoculation, and in general a solution in a sealed tube does crystallise at, or slightly below, this temperature.

The solubility curves for the two series of mixtures have been traced, and found to be approximately straight lines running nearly parallel to the lower part of the supersolubility curve.

Rapid cooling of the solutions has been found to cause them to pass into the labile state before the shower of crystals appears, but prolonged heating of the solutions did not appear to affect their behaviour.

The introduction of an excess of crystals into a metastable solution relieves the supersaturation and prevents the solution from becoming labile and reaching the supersolubility curve.

In some of the solutions of the first series of experiments containing from 45 to 49·5 per cent. of sodium nitrate, after the shower of crystals has appeared the fall in index is sometimes oscillatory, rising a little and then falling again.

In conclusion, I desire to express my thanks and gratitude to Professor H. A. Miers for his valuable advice and continual assistance given me throughout the course of this research.

Mineralogical Department,
University Museum,
Oxford.

XXXVIII.—*Amphoteric Metallic Hydroxides. Part I.*

By John Kerfoot Wood.

Much interest has been taken of late in amphoteric compounds, especially in the behaviour of such substances as are electrolytes. The divergence from Ostwald's dilution law and the other abnormalities exhibited by these substances have been explained by Walker (*Proc. Roy. Soc.*, 1904, **74**, 155; *Zeitsch. physikal. Chem.*, 1904, **49**, 82). The substances hitherto examined have been almost wholly of an organic nature, and necessarily so, for very few inorganic substances are of the nature of amphoteric electrolytes. It is well known, however, that many metallic hydroxides possess an amphoteric character, although they cannot, owing to their very slight solubility, be termed electrolytes, and it appeared to the author that an examination of these substances and a comparison of their basic and acidic constants would be of interest. When arsenious oxide dissolves in water, a certain quantity passes into arsenious hydroxide. The results obtained with this substance, which was chosen as being a soluble amphoteric hydroxide, and aluminium hydroxide, a typical insoluble amphoteric hydroxide, form the subject of the present paper. Other hydroxides are at present under examination, and the results obtained will form the subject of future communications.

Arsenious Hydroxide Regarded as a Base.—A consideration of the properties of this compound makes it at once obvious that its basicity must be of a very low order of magnitude. Zawidzki (*Ber.*, 1903, **36**, 1427), in fact, after examining various arsenic compounds, arrived at the conclusion that the hydroxide is practically devoid of basic character. It was thought that by adopting the Löwenherz solubility method some light on the subject might be obtained, and accordingly the solubility of arsenious oxide in water and in hydrochloric acid was determined.

Solubility of Arsenious Oxide in Water.—Very divergent figures have been published for the solubility of arsenious oxide in water. The matter has been complicated by the existence of several varieties of the compound, and also by the fact that the amorphous variety undergoes slow transformation into the octahedral form. In the present experiments, the oxide used was of the octahedral variety, and for the final experiments was specially purified by dissolving in concentrated hydrochloric acid, diluting with water, and filtering and washing the crystals which were deposited.

The solubility was determined as follows: a mixture of the oxide and distilled water was placed in a bottle made of "resistance-glass," which was then attached to a shaking machine. At intervals, portions were filtered off and titrated with a decinormal solution of iodine. The shaking was continued until the titre of the filtered solution was constant, and the solubility was then calculated from the final titre. All the experiments were made at the laboratory temperature of 15° (approx.).

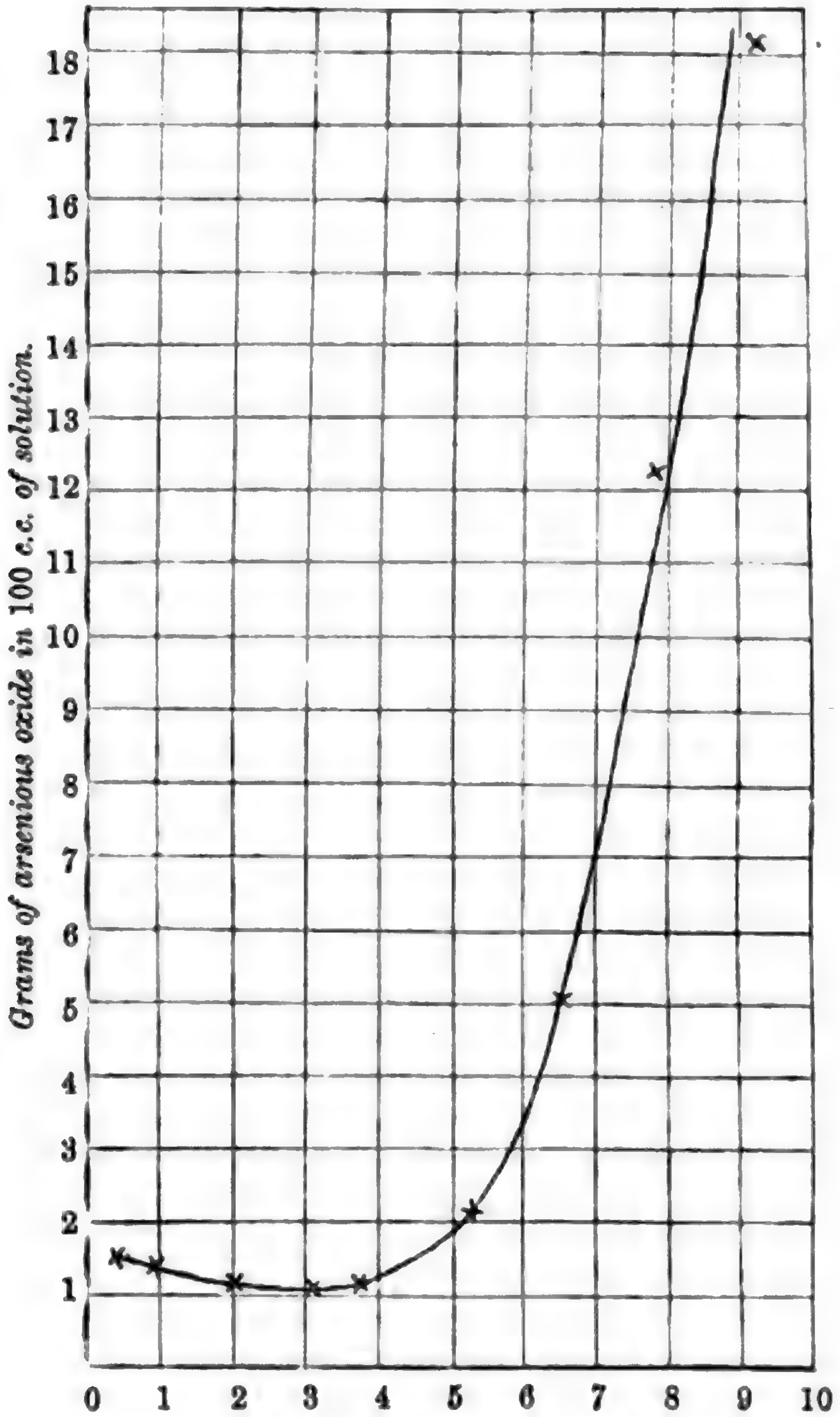
In the preliminary experiments, the solubility obtained was 1·55 grams per 100 c.c. of water; using the specially purified substance, the result was of only slightly different value, concordant determinations showing that 100 c.c. of water dissolve 1·495 grams of arsenious oxide. A saturated solution was obtained only after shaking for several weeks.

Solubility of Arsenious Oxide in Hydrochloric Acid.—The method of determination was similar to that described above for the solubility in water, the arsenious oxide being mixed with solutions of hydrochloric acid of varying concentration. The concentration of the acid solvent was determined by titrating a portion of the solution with sodium hydroxide, using methyl-orange as indicator. The time necessary for the attainment of saturation was much shorter than in the case of the aqueous solution. In most of the experiments, the oxide and acid were in contact for about twenty-four hours. This period was longer than necessary, time experiments having shown that the solution became saturated after several hours' shaking. The author thus confirmed the observation of Drucker (*Zeitsch. physikal. Chem.*, 1901, **36**, 173), that the rate of dissolution of crystalline arsenious oxide is greatly accelerated by the presence of hydrogen ions. The following results were obtained:

Concentration of hydrochloric acid.	Grams of arsenious oxide per 100 c.c. of solution.	Concentration of arsenious oxide.
0·46*N*	1·52	0·051*N*
0·98*N*	1·41	0·047*N*
2·03*N*	1·17	0·039*N*
3·13*N*	1·11	0·037*N*
3·81*N*	1·13	0·038*N*
5·32*N*	2·20	0·074*N*
6·50*N*	5·11	0·17*N*
7·85*N*	12·28	0·41*N*
9·17*N*	18·16	0·61*N*

From a consideration of the above table, it is evident that in hydrochloric acid of less than seminormal concentration the solubility of arsenious oxide is about equal to its solubility in pure water. As the concentration of the acid increases, the solubility of the oxide decreases, a minimum being reached when the concentration of the solvent is about 3·2*N*. Beyond this point, an increase in the concentration of the solvent leads to a corresponding increase in the solubility. The variation of the solubility of arsenious oxide with the concentration of the hydrochloric acid used as solvent is shown in the accompanying curve, which illustrates very clearly the difference between the basic and acidic constants of arsenious hydroxide. It is obvious that the introduction of hydrochloric acid into the system of water and arsenious hydroxide will cause a decrease in the acidic ionisation of the latter, and consequently a diminution in the solubility of the arsenious oxide. On the other hand, the addition of hydrochloric acid will increase the solubility of arsenious hydroxide as a base. Whether the increase or decrease in the solubility is the greater is partly dependent on the respective magnitudes of the basic and acidic constants of arsenious hydroxide, and partly on the amount of hydrochloric acid added. From the fact that the first effect of the addition of hydrochloric acid is to cause a steady fall in the solubility, it is at once evident that the acidic dissociation constant of arsenious hydroxide must be much greater than the basic constant. It is only when the hydrogen ions, introduced in the form of hydrochloric acid, have reached such a concentration as to make the acidic ionisation of the arsenious hydroxide impossible, that it becomes possible to see the effect which a further increase in the concentration of the hydrochloric acid has on the solubility of arsenious oxide in virtue of the basic character of the hydroxide. Beyond the minimum of the curve, the increase in the solubility can only be accounted for on the assumption that arsenious hydroxide possesses feeble basic properties. By extrapolation of this portion of the curve, a value for the solubility in water, eliminating that portion of the ordinary solubility due to the acidic dissociation, can be obtained. Using this number and applying the Löwenherz method, a

FIG. 1.



value for $\frac{k_b}{K}$ of the dimensions of 1 is arrived at. Consequently, the basic dissociation constant of arsenious hydroxide is of the dimensions 1×10^{-14}.

Arsenious Hydroxide Regarded as an Acid.—From the fact that an aqueous solution of arsenious oxide possesses a very feeble acid reaction, it may be safely assumed that the acidic constant is higher than the basic one, although the fact that solutions of sodium and potassium arsenites possess a strongly alkaline reaction shows that even the acidic constant can have only a small value.

The acidic constant was determined from the velocity with which methyl acetate was saponified by a solution of sodium arsenite (Shields, *Zeitsch. physikal. Chem.*, 1893, **12**, 167; Wood, Trans., 1906, **89**, 1832). A solution of sodium metarsenite was prepared by dissolving a weighed quantity of re-sublimed arsenious oxide in the calculated amount of 0·0495*N* sodium hydroxide. Equal amounts of this solution and of a solution of methyl acetate of the same concentration were mixed, and the mixture maintained at a temperature of 25°. Portions of the mixture were removed at intervals, and titrated with 0·01*N* hydrochloric acid; the velocity constant was calculated by means of the equation given in a previous paper (Wood, *loc. cit.*). The results of one determination are given below:

20 c.c. 0·0495*N* sodium metarsenite + 20 c.c. 0·0495*N* methyl acetate.

Time.	Titre.	*k*.
0	10·05	—
284	7·25	0·000212
1356	5·10	0·000216
	Mean............	0·000214

This value for *k* was confirmed by several other experiments. Using the above figure for the velocity constant, the calculated value for k_a, the dissociation constant of arsenious acid, is found to be $6·3 \times 10^{-10}$. Knowing the velocity constant, the hydrolysis constant of sodium metarsenite, and consequently the amount of hydrolysis, can also be calculated (compare Wood, *loc. cit.*). In decinormal solution, it is found that sodium metarsenite is hydrolysed at 25° to the extent of 1·4 per cent.

Electrical Conductivity of Aqueous Solutions of Arsenious Oxide.—Zawidzki (*loc. cit.*) determined the conductivity of aqueous solutions of arsenious oxide and thence calculated the dissociation constant, obtaining a value for the latter of 210×10^{-10}. In view of the divergence between this number and the value of the acidic constant determined by the author, it was decided to make a re-determination of the dissociation constant by means of the conductivity method. Arsenious oxide was crystallised from specially distilled conductivity water, and the crystals obtained were repeatedly washed with similar water, a solution of the washed crystals being afterwards prepared. All the operations incidental to the preparation of the solution were carried out in the open air.

The concentrated solution so obtained was diluted to different extents with conductivity water, a fresh portion of the concentrated solution being used for each dilution. The conductivity of the dilute solutions was then determined, using unplatinised electrodes, after which the concentration of the various solutions was ascertained by titration with decinormal iodine solution.

The water used for the experiments had a conductivity of 1×10^{-6} at 25°. All conductivities are expressed in reciprocal ohms.

Results of First Series of Experiments:

Concentration of solution of metarsenious acid.	μ.	k.
0·1755*N*	0·0556	$35{\cdot}2 \times 10^{-10}$
0·089*N*	0·0656	$24{\cdot}8 \times 10^{-10}$
0·0365*N*	0·105	$26{\cdot}1 \times 10^{-10}$

Results of Second Series of Experiments.—The experiments of this series were made with a sample of purified arsenious oxide different from that employed in the first series:

Concentration of solution of metarsenious acid.	μ.	k.
0·195*N*	0·0553	$38{\cdot}6 \times 10^{-10}$
0·086*N*	0·0654	$23{\cdot}9 \times 10^{-10}$
0·0542*N*	0·0756	$20{\cdot}1 \times 10^{-10}$
0·0385*N*	0·0824	$16{\cdot}9 \times 10^{-10}$

The mean value of the above results is $26{\cdot}5 \times 10^{-10}$, a number considerably smaller than that obtained by Zawidzki, although still greater than that arrived at by the saponification method.

Probably this discrepancy may be explained by the arsenious oxide still containing a small quantity of conducting impurity; the fact, however, that very similar values for k were obtained in the two series of experiments shows that the amount of this impurity must have been very small. The difficulty of removing the last traces of impurity from a substance has been noticed by Johnston (compare Walker, *Proc. Roy. Soc.*, 1904, **74**, 278) in the case of asparagine, the dissociation constant of which is of similar magnitude to that of arsenious acid. Moreover, no attempt was made to exclude air from the cell. Had this been done, as in the case of Walker and Cormack's experiments with weak acids (Trans., 1900, **77**, 5), the discrepancy between the results obtained by the two methods might have been smaller. Comparing the results obtained by the author with those arrived at by Walker and Cormack (*loc. cit.*) and allowing for the difference in temperature, arsenious acid is found to be of about the same strength as boric acid.

Aluminium Hydroxide.

This compound, like arsenious hydroxide, is of an amphoteric nature. The two substances are, however, of distinctly different types, for, whereas with the arsenious hydroxide it is the acid properties which are the more highly developed, in the case of the aluminium hydroxide it is the basic properties which are the stronger. Another important difference between the compounds is in their behaviour towards water, in which aluminium hydroxide is practically insoluble. This fact considerably increases the difficulty of investigating the amphoteric nature of the compound, and also renders it impossible to determine its conductivity.

Aluminium Hydroxide Regarded a a Base.—It is a well-known fact that the aluminium salts undergo hydrolysis in aqueous solution, and it was therefore evident that one method of arriving at a knowledge as to the basic constant of the hydroxide would be by the determination of the amount of this hydrolysis. For this purpose, a concentrated aqueous solution of aluminium chloride was prepared and slowly evaporated in a vacuum over sulphuric acid. The crystals of pure aluminium chloride ultimately obtained were washed with distilled water, and a solution then prepared. The concentration of this solution was determined by estimating the chlorine by Volhard's method. The velocity with which this solution hydrolysed methyl formate at 25° was then determined, and compared with the velocity obtained using $N/100$ hydrochloric acid. The use of methyl formate in such experiments has been suggested by Goldschmidt, and it was employed in the present case in preference to methyl acetate because the reaction proceeds with much greater velocity than is the case with the latter substance. It might be anticipated that, owing to the dissociation constant of formic acid being much greater than that of acetic acid, the use of methyl formate under the conditions of the experiment would be inadmissible. Preliminary experiments showed, however, that by reducing the ratio of ester to solution this difficulty was eliminated. In the actual experiments, 200 c.c. of the solution were mixed with 1 c.c. of methyl formate. The following results were obtained:

With $N/100$ hydrochloric acid, velocity of reaction $= 0{\cdot}000661$.

With aluminium chloride ($\mathrm{Cl} = 0{\cdot}1127N$), velocity of reaction $= 0{\cdot}000100$.

It is therefore evident that the concentration of the hydrochloric acid present in the solution of aluminium chloride was $0{\cdot}0015N$.

The amount of hydrolysis, that is, the percentage of the aluminium chloride existing either as hydroxide or basic chloride, is dependent on the mode of decomposition of aluminium chloride by water. As will be seen from the following equations, this decomposition can take place in three ways, namely:

$$\begin{aligned} AlCl_3 + H_2O &= Al(OH)Cl_2 + HCl \quad (1) \\ AlCl_3 + 2H_2O &= Al(OH)_2Cl + 2HCl \quad (2) \\ AlCl_3 + 3H_2O &= Al(OH)_3 \quad + 3HCl \; (3). \end{aligned}$$

It is evident that the ratio between the amount of aluminium chloride decomposed and the quantity of hydrochloric acid liberated, measured by the hydrolysis of methyl formate, is different in these three reactions. Therefore, according as to whether the mode of decomposition is represented by equation (1), (2), or (3), the amount of hydrolysis of the aluminium chloride will be $\frac{0{\cdot}0015 \times 3}{0{\cdot}1127}$, $\frac{0{\cdot}0015 \times 3}{0{\cdot}1127 \times 2}$, or $\frac{0{\cdot}0015 \times 3}{0{\cdot}1127 \times 3}$ respectively, that is, 4 per cent., 2 per cent., or 1·33 per cent.

It is difficult to say which equation accurately represents the change taking place, for no decomposition product can be separated and analysed. It may even be the case that a mixture of basic compounds is present in the solution, in which case no single equation would represent the reaction. Now, considering the ionisation of aluminium hydroxide, it is to be expected that, following the general rule, there will be a great disparity in the strengths of the three hydroxyl ions, the first being much stronger than the second, and the second stronger than the third. It is by virtue, first of all, of the weakest of these hydroxyl ions that hydrolysis of the chloride takes place, leading to the formation of the basic chloride, $Al(OH)Cl_2$. As the amount of hydrolysis is only small, it seems probable that the action stops here and that no more highly basic compound is produced. On theoretical grounds, therefore, it seems probable that the reaction taking place during the hydrolysis of aluminium chloride is represented by equation (1).

With the object of gaining further knowledge on this subject, experiments were made in which freshly-precipitated aluminium hydroxide was shaken with hydrochloric acid of varying concentration. Equilibrium was attained after several days' shaking, the solution obtained by filtering off the undissolved hydroxide showing no change of composition even when the shaking was prolonged. In nearly the whole of the experiments, the ratio of atoms of aluminium to atoms of chlorine lay between 1 : 2 and 1 : 3, but the results of different series of experiments were not strictly concordant. It was thought that the lack of uniformity in the results might possibly be explained by the presence in the various solutions of varying amounts of colloidal aluminium hydroxide. It is well known that substances in colloidal solution are frequently precipitated on the addition of ammonium sulphate, and the experiment was tried of adding varying amounts of that salt to the solutions obtained as described above. No change in the composition of the solutions resulted from such additions, and the addition of barium sulphate to the solution, as suggested by Fischer (*Zeitsch. anorg. Chem.*, 1904, **40**, 39), was also without effect. It seems probable, therefore, that all the aluminium was present in a state of true solution, and that the slight variations in the composition of such solutions are due to their containing the normal and basic aluminium chlorides in varying proportions, the variation being possibly due to some slight, but undetected, differences in the conditions of the experiments. The composition of the mixture being of a variable nature, no deductions as to the hydrolysis of aluminium chloride can be drawn from the analysis of the mixtures obtained in different experiments.

It would therefore appear to be probable that in a solution of aluminium chloride containing 0·0375 molecule of salt per litre, the hydrolysis at 25° amounts to about 4 per cent. As, however, the mode of hydrolysis cannot be experimentally proved to take place according to the equation $AlCl_3 + H_2O = Al(OH)Cl_2 + HCl$, no attempt was made to determine the basic constant of aluminium hydroxide from the amount of hydrolysis.

Aluminium Hydroxide Regarded as an Acid.—The fact that alumina can play the part of an acidic oxide is evident from the existence of such minerals as spinel and chrysoberyl, and from the possibility of obtaining solid alkaline aluminates from the solutions of aluminium hydroxide, and also of metallic aluminium in solutions of the caustic alkalis. In the majority of chemical textbooks, the compound formed when either aluminium or aluminium hydroxide is dissolved by a solution of sodium hydroxide is assigned the formula Na_3AlO_3. The results obtained by the author, however, point to the substance being really the metaluminate, $NaAlO_2$. The naturally occurring salts are also metaluminates, for example, $Mg(AlO_2)_2$, $Zn(AlO_2)_2$, $Be(AlO_2)_2$. Moreover, by the addition of calcium chloride to a solution of sodium aluminate, a precipitate is obtained which consists of calcium metaluminate, $Ca(AlO_2)_2$. It seems probable, therefore, that the compounds in which alumina acts as an acidic oxide are generally salts of an acid of the formula $HAlO_2$, although under certain conditions it may be possible to prepare ortho-salts. The conclusion is in complete agreement with that arrived at from general considerations. It is well known that, in the case of weak polybasic acids, it is the first hydrogen atom to which most of the acidity is due. The same course, it may be expected, will be followed in the case of aluminium hydroxide, which is an extremely weak acid. Practically the whole of the dissociation will be into the ions H and AlO_3H_2, or AlO_2,H_2O, so that the stable salts will be those containing one equivalent of metal.

Action of Sodium Hydroxide on Aluminium.

Aluminium powder was added to an aqueous solution of pure sodium hydroxide, the mixing taking place in a large flask made of "resistance-glass" and fitted with a soda-lime tube so as to protect the contents of the flask from atmospheric carbon dioxide. A vigorous reaction soon commenced, the mixture frothing considerably. After a short time, the frothing ceased and any further action which took place proceeded very quietly. In several cases, in order to ensure equilibrium, the alkali and metal were left in contact for several days, but the results obtained in these experiments were no different from those given by experiments in which the contact between alkali and metal was of only a few hours' duration. The mixture was then filtered and the filtrate analysed, the aluminium being determined by precipitation with ammonium chloride, and the alkali by boiling with ammonium chloride and estimating the ammonia evolved:

Results of Analyses.

	NaOH per litre of solution.	Al_2O_3 per litre of solution.	Mols. of NaOH : mols. of Al_2O_3.
A.	11·04	12·32	2·28 : 1
B.	10·78	11·90	2·31 : 1
C.	18·36	20·04	2·34 : 1

It will be observed that in every case the solutions contained rather more alkali than was necessary to convert the aluminium into sodium metaluminate, the results obtained being quite incompatible with the formation of an ortho-salt. A slight excess of alkali over the amount required to form the metaluminate is to be expected, because of the partial hydrolysis of the salt.

Equilibrium between Aluminium Hydroxide and Sodium Hydroxide.

In order to gain some idea as to the constitution of the salt formed when aluminium hydroxide dissolves in a solution of sodium hydroxide, a solution of aluminium sulphate of known strength was added to *N*-sodium hydroxide until a slight permanent precipitate was obtained. For 20 c.c. of *N*-sodium hydroxide, a volume of aluminium sulphate solution equivalent to 0·2458 gram of alumina was required to give a faint permanent precipitate. Of the sodium hydroxide present, 0·5784 gram would be required to precipitate the aluminium hydroxide, leaving 0·2216 gram to dissolve the latter. From these figures, we obtain the ratio:

Mols. of sodium hydroxide : Mols. of aluminium hydroxide = 2·30 : 1.

It will be observed that the result is in complete agreement with those obtained when metallic aluminium was dissolved in sodium hydroxide, and shows that in this case, also, the salt in solution was the metaluminate.

Behaviour of Solutions of Sodium Metaluminate.

The solutions prepared by the action of sodium hydroxide on aluminium powder were comparatively stable at the ordinary temperature, aluminium hydroxide being deposited very slowly. On heating, however, decomposition took place much more rapidly. In the case of solution *A* (see p. 420), after heating for two hours on the water-bath, the ratio of molecules of alkali to molecules of aluminium hydroxide had increased from 2·28 to 3·63. It appeared as if a state of equilibrium had been attained, for no further deposition of aluminium hydroxide took place when the liquid was re-heated. The fact that a state of equilibrium could be reached in this way suggested that the method might be made use of to determine the degree of hydrolysis of sodium metaluminate. The principle of the method is really that of the Löwenherz solubility method. In the Löwenherz method, the hydrolysis constant of the salt is calculated by means of the equation:

$$\frac{\text{Acid} \times \text{Base}}{\text{Salt}} = \text{constant}.$$

The same equation will, of course, hold good in the case of sodium metaluminate, but the concentration of the acid cannot be directly determined, the solubility of aluminium hydroxide in water being too small to permit of direct determinations being made. By equating the results of two equilibrium experiments, however, it is possible to obtain a theoretical value for the solubility of metaluminic acid, and therefore to calculate the value of the hydrolysis constant.

If x is the concentration of metaluminic acid, a_1 and a_2 the total concentrations of aluminium as determined from two equilibrium experiments, and b_1 and b_2 the total concentrations of alkali in the same two experiments,

then $$\frac{x(b_1 - a_1 + x)}{a_1 - x} = \text{constant and } \frac{x(b_2 - a_2 + x)}{a_2 - x} = \text{constant}.$$

The constants being the same in the two cases, the left-hand sides of the equations may be equated, giving:

$$\frac{x(b_1 - a_1 + x)}{a_1 - x} = \frac{x(b_2 - a_2 + x)}{a_2 - x},$$

whence
$$x = \frac{a_2 b_1 - a_1 b_2}{b_1 - b_2}.$$

By substituting this value of x in either of the original equations, the numerical value of the hydrolysis constant is found, and, knowing this, it is possible to calculate the amount of hydrolysis which would take place in a solution of any concentration.

The following results were obtained on analysing solutions of sodium metaluminate which had been heated on the water-bath until equilibrium was attained:

	Weight of NaOH per litre.	Weight of Al_2O_3 per litre.	Mols. of NaOH.	Mols. of $HAlO_2$.
a.	10·08	7·10	0·252	0·139
b.	18·36	10·86	0·459	0·213
c.	9·00	6·65	0·225	0·130
d.	5·55	4·87	0·138	0·0955

From the above results, taking them in pairs, the value of the hydrolysis constant was calculated, and from that the amount of hydrolysis which would take place in a decinormal solution of sodium metaluminate was determined. The following were the figures obtained:

From (*a*) and (*b*)	59·5	From (*b*) and (*c*)	60·6
,, (*a*) ,, (*c*)	63·4	,, (*b*) ,, (*d*)	57·2
,, (*a*) ,, (*d*)	55·0	,, (*c*) ,, (*d*)	52·4

Mean = 58·0.

The above figures certainly show a considerable variation, but, when it is remembered that a very slight experimental error has a large influence on the value of the hydrolysis constant, results of normal constancy can scarcely be expected. Probably no appreciable error will be committed in stating that a decinormal solution of sodium metaluminate is hydrolysed to the extent of 60 per cent. at 100°.

Similar equilibrium experiments were carried out at 25°. In these experiments, equilibrium was attained very slowly, a period of about four weeks being necessary for the solutions to attain constancy of composition. The following results were obtained:

	Mols. of NaOH	Mols. of $HAlO_2$.
a.	0·249	0·0615
b.	0·343	0·0829
c.	0·228	0·0568

As before, the amount of hydrolysis in a decinormal solution was calculated and the following values were obtained:

From (*a*) and (*b*)	33·3
,, (*a*) ,, (*c*)	38·1
,, (*b*) ,, (*c*)	34·3
Mean =	35·2

A decinormal solution of sodium metaluminate is therefore hydrolysed to the extent of 35 per cent. at 25°.

Now the hydrolysis constant $= K/k_a$, where K is the dissociation constant of water and k_a that of metaluminic acid. The value of the hydrolysis constant, assuming a decinormal solution to be 35 per cent. hydrolysed, is 0·0188, whilst K at $25° = 1{\cdot}2 \times 10^{-14}$.

From these figures, it is found that the acidic dissociation constant of aluminium hydroxide (k_a) has a value of $6{\cdot}3 \times 10^{-13}$.

Summary of Results.

The solubility of arsenious oxide in hydrochloric acid first diminishes as the concentration of the acid increases. A minimum is reached when the acid has a concentration of about 3·2*N*. Beyond this point, a further increase in the concentration of the acid causes an increase in the solubility.

Arsenious hydroxide is a very feeble base, the basic constant being of the dimensions of 1×10^{-14}. The acidic constant, as found by the saponification method, has a value of $6{\cdot}3 \times 10^{-10}$, and a decinormal solution of sodium metarsenite is hydrolysed to the extent of 1·4 per cent at 25°. The dissociation constant of arsenious acid as found by the conductivity method has a value of $26{\cdot}5 \times 10^{-10}$.

Aluminium hydroxide is a weak base. The chloride is hydrolysed to the extent of about 4 per cent. at 25°, and is probably transformed into a basic chloride having the formula $Al(OH)Cl_2$. Sodium metaluminate in decinormal solution is hydrolysed to the extent of about 35 per cent. at 25°, the acidic constant of aluminium hydroxide being $6{\cdot}3 \times 10^{-13}$.

University College,
Dundee.

XXXIX.—*Anomalous Behaviour of the Hydrogen-Electrode in Solutions of Lead Salts, and the Existence of Univalent Lead Ions in Aqueous Solutions.*

By Henry George Denham, M.A., M.Sc., and Arthur John Allmand, M.Sc.

An attempt was made to measure the hydrolysis of lead salts by the electrometric method described by one of us (Trans., 1908, **93**, 41). Solutions of lead chloride, sulphate, and acetate were experimented with, but in every case it was noticed that the electrode did not attain a steady value in the usual time (ten minutes), and even after some hours it had not reached a value such as would be expected from Ley's measurements on the hydrolysis of lead chloride by the inversion method (*Zeitsch. physikal. Chem.*, 1899, **30**, 193). For instance, a solution of lead acetate, which reacted alkaline to litmus, gave after two hours a hydrogen-ion concentration of the order 10^{-4}, whereas one would expect a value not greater than 10^{-9}. In fact, the value found for the hydrolysis was in all cases far higher than was expected.

Two possible explanations suggested themselves, firstly, the separation from the solution of a metal more "noble" than hydrogen, and, secondly, the possibility that lead itself might be precipitated on the electrode when the current passed in such a way that the hydrogen-electrode was acting as a cathode.

The first possibility was disproved by using a solution of very pure lead chloride, previously boiled with lead clippings, to remove silver or any other metals more "noble" than lead. This solution behaved in exactly the same manner as the others.

The possibility of deposited metallic lead causing the phenomenon was disposed of by two experiments. A few milligrams of metallic lead were deposited on a hydrogen-electrode, which was then tested in $0{\cdot}001\,N$-hydrochloric acid; the potential registered showed that the lead had in no way altered the character of the electrode, which behaved exactly as an ordinary hydrogen-electrode. Lastly, an experiment was carried out in which the hydrogen-electrode always acted as anode, but precisely similar results were obtained.

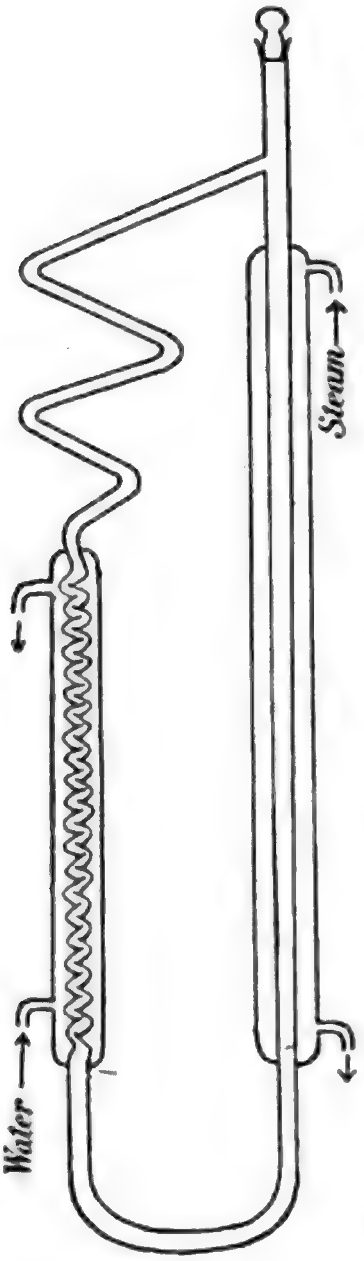
Although the above experiments conclusively prove that lead itself cannot cause the phenomenon, there yet remains the possibility that lead-platinum alloys may be formed, in which the lead, on the analogy of the osmotic pressure of mixed crystals, has a lower solution pressure than that of pure lead, and, perhaps, of hydrogen itself, and hence may be precipitated as alloy by the latter. But it was noticed that the potential obtained depended on the velocity with which the hydrogen bubbled through the solution; the quicker the stream the lower the hydrogen potential, and vice versa. Now each bubble of gas rose from directly beneath the electrode, consequently the faster the stream of gas the more would the surface film of the electrode be disturbed. This suggested that the action $Pb^{\cdot\cdot} + H \rightleftarrows Pb^{\cdot} + H^{\cdot}$ was occurring in the surface film; the faster the stream of gas the more quickly would the free acid, produced through the reduction of bivalent to univalent lead ions, be carried into the main bulk of the liquid, and, hence, the lower would be the hydrogen potential. This consequence was tested by shaking the electrode, when the same effect was observed as on increasing the velocity of the gas, and also by arranging in the same solution two electrodes differently situated as regards the incoming gas. There was a marked difference in the potentials recorded by these electrodes, that directly above the place where the gas entered giving a decidedly lower value than was given by the electrode which was further removed from the disturbing influence of the hydrogen. These facts are sufficient evidence to disprove the formation of such an alloy as already described.

Thus the anomalous behaviour of the hydrogen-electrode in solutions of lead chloride, sulphate, and acetate seems best explained on the assumption that the hydrogen-electrode reduces the bivalent to a univalent lead ion with the production of free acid, and the potential registered is that of the surface film, rich in the hydrogen ion.

The existence of $Pb^{\cdot}$-ion in solution has not previously been noticed, but the existence of lead sub-oxide (Pb_2O) has been rendered tolerably certain by the experiments of Tanatar (*Zeitsch. anorg. Chem.*, 1901, **27**, 304), recently confirmed by Brislee (Trans., 1908, **93**, 154).

The discrepancy observed in the use of the copper voltameter has been definitely proved to be attributable to the formation of cuprous salts in solution. The silver voltameter shows a similar behaviour, and Bose (*Zeitsch. Elektrochem.*, 1907, **13**, 477) has shown that a subvalent silver ion can exist in solution. To test the possibility of a univalent lead ion, the method described by Richards, Collins, and Heimrod (*Zeitsch. physikal. Chem.*, 1900, **32**, 321) for copper, and by Bose (*loc. cit.*) for silver, has been used. This is based on the fact that the formation of the sub-salts of copper and silver is attended by the absorption of heat. On heating the metal in contact with a solution of its salt, the equilibrium shifts towards the sub-salt, whilst, on cooling, the process reverses and metal is precipitated.

The apparatus used is shown in the figure. The right limb contained a column of pure granulated lead surrounded by a steam-jacket, whilst the left spiral limb was kept cool by a stream of cold water. In this way, a constant circulation of the solution contained in the apparatus is kept up by the differences of density occasioned through the difference in temperature between the two limbs. The apparatus contained a 1·3 molar-normal solution of lead acetate slightly acidified with acetic acid. After a few days, distinct crystals of lead began to appear on the glass at the bottom of the hot limb, and these grew steadily, forming quite a network of shining crystals. Nothing, however, appeared in the cold limb, where crystallisation was expected, but, on introducing a piece of lead into the top of the spiral condenser, well-defined crystals soon made their appearance on it, and these steadily increased in size. This proves that the solution in the cold limb was supersaturated with the univalent ion, for, unless crystallisation is started by introducing a piece of lead, no crystals appear until the solution reaches the cold end of the column of lead.



Although the crystals obtained in the cold limb can only be due to the reaction $Pb^{\cdot\cdot} + Pb \longrightarrow 2Pb^{\cdot}$ having taken place in the hot limb, and being reversed in the cold, still it is possible that the crystals at the bottom of the lead column were due to a weak thermo-current flowing from the hot solution above to the comparatively cold solution at the bottom of the limb, for it is evident that the solution would not immediately attain the temperature of the jacket.

This possibility was tested in two ways. In the first case, an experiment was devised in which there were present all the conditions for such a thermo-electric current, but the cumulative effect due to the circulation was dispensed with. The apparatus consisted of a glass tube sealed at one end. It contained a rod of lead and a molar-normal solution of lead acetate, acidified with acetic acid. The upper part of the tube was enclosed by a steam-jacket, the lower was at the ordinary temperature. All the conditions for a thermo-current present in the former experiment are satisfied here, but, owing to the want of circulation, there is little chance of univalent lead ions formed in the upper and hot portion diffusing to the cold end in sufficient quantity to cause any marked crystallisation.

At the end of a week, the experiment was stopped, and the rod of lead examined. At the junction of the hot and cold parts of the lead, a very little spongy lead had been deposited. The quantity so obtained was far less than that in the former experiment, and totally different in appearance. Thus it is definitely proved that a slight thermo-current from the hot solution above to the colder beneath does exist, but the lead deposited is not only much too small in quantity to explain that deposited at the bottom of the lead column in the "circulation" experiment, but is also of the spongy nature with which we are familiar in the electrolysis of solutions of many lead salts.

Moreover, the thermo-electric theory was again disproved by repeating the "circulation" experiment with one altered condition; the lead column was broken by glass beads into a number of short sections, between the ends of which there could be no appreciable difference. Yet, after two days, crystals of lead began to appear, and in a short time formed a network round the whole of the bottom section. Rapid crystallisation also took place on a piece of lead introduced into the top of the cold condenser.

We are therefore justified in concluding that in the "circulation" experiments the whole of the crystalline lead deposited is due to the reaction $Pb^{\cdot\cdot} + Pb \longrightarrow 2Pb^{\cdot}$ taking place in the hot, but reversing in the cold, and, moreover, the presence of a univalent lead ion in aqueous solution has for the first time been proved.

Summary.

1. The hydrogen-electrode cannot be used to determine the hydrolysis of lead salts, owing to the reduction of the bivalent to the univalent lead ion.
2. A solution of lead acetate, heated with lead, forms a sub-acetate, and this is attended with the absorption of heat.
3. A piece of lead in a solution of lead acetate, which is maintained at two different temperatures, forms a thermo-cell, the current flowing from the hot solution to the cold, and causing the deposition of traces of spongy lead at the cold end of the column of lead.

In conclusion, we wish to take this opportunity of thanking Prof. F. G. Donnan for the interest he has displayed in these experiments.

THE MUSPRATT LABORATORY OF
PHYSICAL AND ELECTRO-CHEMISTRY,
UNIVERSITY OF LIVERPOOL.

XL.—*The Preparation of Conductivity Water.*

By Harold Hartley, Norman Phillips Campbell, and
Reginald Holliday Poole.

As a preliminary to some work on dilute aqueous solutions, we have investigated the efficiency of a number of different ways of preparing conductivity water, with a view to finding a trustworthy method which gives water with a specific conductivity not greater than 1 gemmho ($1{\cdot}0 \times 10^{-6}$ reciprocal ohms) when carried out in a chemical laboratory under ordinary conditions. The difficulty of the operation depends somewhat on the quality of the water supply, and in this respect Oxford water is bad, as it is hard and gives carbon dioxide on distillation.

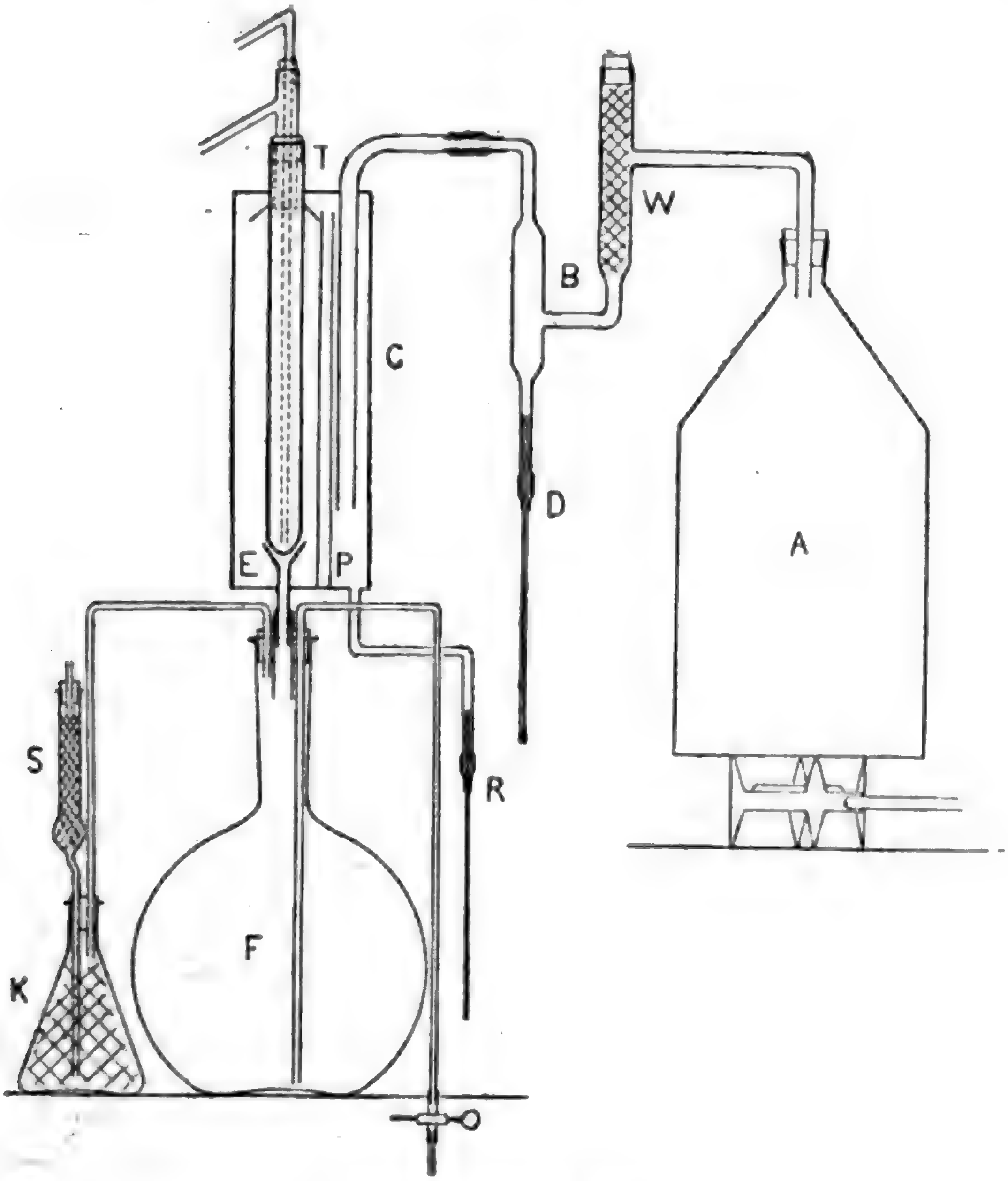
With the still described below, we have no difficulty in making two and a-half litres of water, $K_{18} = 0{\cdot}75$ gemmho, and three more litres of fairly good water, $K_{18} = 1{\cdot}5$ gemmhos, in a single distillation of ordinary distilled water, carried out in a laboratory without any special precautions to keep the air free from impurities.

The present form of the apparatus is the outcome of a number of suggestions gathered from other laboratories, and it has no claims to originality. We are greatly indebted to Professor James Walker for valuable advice which solved most of our difficulties, to Mr. Bousfield's paper which suggested to us the form of the condenser, and also to Dr. Lowry and to Mr. J. J. Manley.

The general plan of the apparatus is shown in the diagram on p. 429.

The boiling vessel, *A*, is of copper or tinned iron, holding about ten litres. From *A*, the steam passes through the glass trap, *B*, where any dust is stopped by the glass wool, *W*, and any condensed water escapes at *D*. The steam then passes into the condensing vessel, *C*, which is made of the best tinned iron. The condenser tube, *T*, is made of block tin, soldered through the lid; it is cooled internally by a stream of tap water. *P* represents baffle plates to prevent the steam carrying over any drops of liquid containing dissolved matter. Water condenses on *T*, and the small tin cover prevents any water, besides that condensed on the block tin surface, from dropping into the tin funnel and delivery tube, *E*. The waste water runs away through *R*. As there is usually a small pressure of steam in the apparatus, it is necessary to attach a fine capillary tube at both *D* and *R* to prevent the steam blowing off. The form of attachment shown in the diagram prevents the capillary being blocked up by particles of dust.

The water is collected in a steamed-out Jena flask, holding three litres. The tin delivery tube passes through a piece of Jena tubing in the rubber cork of the flask, and a small piece of rubber tubing forms an air-tight joint between them. The water is drawn off through a syphon of Jena tubing, and connexion between the flask and the air is made through the soda-lime tube, *S*, to absorb carbon dioxide; the small flask, *K*, contains moist glass wool to prevent any soda-lime dust being carried over. By this means, when the flask *F* is once attached, the interior of the still, condenser, and receiver is entirely cut off from direct communication with the air, and the water is thus protected from contamination.



(Scale ⅛ natural size.)

The operation is conducted as follows: The boiling vessel is filled with ordinary laboratory distilled water ($\kappa_{18} = 5$ gemmhos approx.). For the first half hour after boiling begins, the water is impure, having a conductivity greater than 2 gemmhos; this is rejected.

After half an hour, the large flask, *F*, is attached to the delivery tube, and the water is collected for two hours; this serves to wash out the flask and to carry into solution any impurities in the air contained in it. These two litres, which have $\kappa_{18} = 1{\cdot}5$ to $1{\cdot}7$ gemmhos, are then run off, and during the next three hours the best water collects. This usually amounts to about two and a-half litres, with $\kappa_{18} = 0{\cdot}75$ gemmho. The flask is then removed, the small tube quickly closed with a rubber plug, and the water may be kept ready for use without its conductivity increasing to any extent. By putting another flask under the delivery tube at this stage, another litre may be obtained, with $\kappa_{18} = 1$ gemmho (approx.).

The results of three days' run of the still are given below. On two of these occasions, the air of the laboratory was contaminated badly with acid fumes:

Time from start of boiling. Hours.	Quantity of fraction collected. Litres.	Conductivity of fraction. Gemmhos.
½	0·5	>2·0
2½	2·0	1·7
5½	2·75	0·73
6½	1·0	1·0
1	0·75	>2·0
3	1·5	1·7
6	2·5	0·75
7	1·0	1·3
1	0·75	>2·0
3	2·0	1·5
5¾	2·5	0·76
6¾	1·0	0·9

These results show that the middle portion of the distillate has a very low conductivity, and, as under the same conditions the best water comes over at about the same time in each distillation, it is easy to know when to start collecting.

In the still described by Bousfield (Trans., 1905, **87**, 740), a condenser of similar pattern to ours is used, but in that case four condensing tubes of hard glass are kept at different temperatures by regulating the flow of the water through them. The presence of hot tubes was thought to be necessary for the success of the operation. But as at least four-fifths of the impurities in "gemmho" water are volatile and less soluble in hot water than in cold, the water condensed on the hotter tubes should have had the lowest conductivity. As a matter of fact, the water from the cold tubes was found to be the best. After a number of experiments with condensers of various kinds, it seems to us that the conductivity of water depends very largely on the extent to which it is protected from air, and we attribute the difference in the conductivity of the water condensed on the hot and cold tubes of Bousfield's apparatus to the difference in the rate of condensation in the two cases. The quicker the water condenses, the less it comes in contact with the air, and the less it is contaminated by carbon dioxide and ammonia.

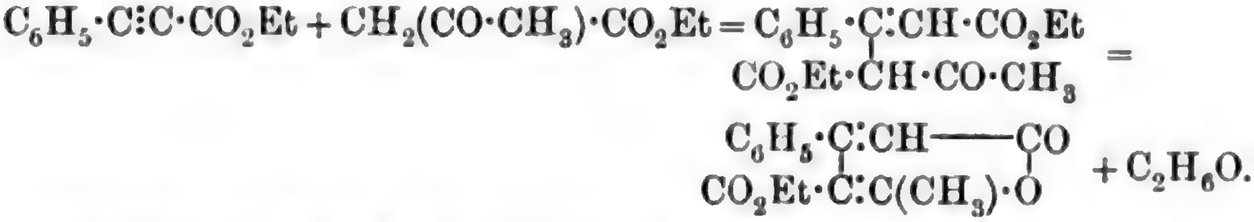
Bousfield's still, in his own laboratory, gave water of $\kappa_{18} = 1{\cdot}1$ to $1{\cdot}2$ gemmhos; if potassium hydrogen sulphate was added to retain ammonia, the best results were $\kappa_{18} = 0{\cdot}96$ to $1{\cdot}1$ gemmhos. In the laboratory of the Central Technical College, at South Kensington, the still gave water with a conductivity $\kappa_{18} = 1{\cdot}7$ gemmhos. The results obtained with the apparatus described in this paper compare very favourably with those just quoted, and the method has the great advantage that the quality of the water is not affected by the presence of impurities in the air of the room in which the distillation is carried out.

Physical Chemistry Laboratory,
Balliol College and Trinity College,
Oxford.

XLI.—*The Formation of 4-Pyrone Compounds from Acetylenic Acids. Part I.*

By Siegfried Ruhemann.

In the course of my studies on the esters of acetylenic acids, it has been shown (Trans., 1899, **75**, 245, 411) that, in the presence of sodium ethoxide, they condense with β-ketonic esters or β-diketones to form 2-pyrone derivatives. For example, ethyl phenylpropiolate reacts with ethyl acetoacetate, thus:



$$C_6H_5\cdot C{\vdots}C\cdot CO_2Et + CH_2(CO\cdot CH_3)\cdot CO_2Et = \begin{array}{l} C_6H_5\cdot C{:}CH\cdot CO_2Et \\ CO_2Et\cdot CH\cdot CO\cdot CH_3 \end{array} = \begin{array}{l} C_6H_5\cdot C{:}CH\text{——}CO \\ CO_2Et\cdot C{:}C(CH_3)\cdot O \end{array} + C_2H_6O.$$

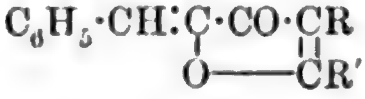
This reaction led to the knowledge of a number of 2-pyrone compounds which, under the influence of ammonia, were transformed into pyridine derivatives.

It appeared of interest to examine whether ketones with the grouping $\cdot CH_2\cdot CO\cdot$ would react with the esters of the acetylenic acids in a manner similar to their action with ethyl oxalate, and yield acetylenic β-diketones:

$$C_6H_5\cdot C{:}C\cdot CO_2Et + HCHR\cdot CO\cdot R' = C_6H_5\cdot C{:}C\cdot CO\cdot CHR\cdot CO\cdot R' + C_2H_6O.$$

(R and R′ denote hydrocarbon radicles.)

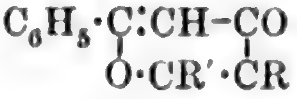
From previous work on the behaviour of organic bases towards acetylenic compounds (Ruhemann and Stapleton, Trans., 1900, **77**, 239), it was to be expected that such diketones would condense to a five- (I) or a six- (II) membered ring:



$$\begin{array}{l} C_6H_5\cdot CH{:}C\cdot CO\cdot CR \\ \qquad\qquad O\text{———}CR' \end{array}$$

(I.)

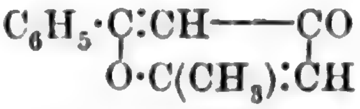
or



$$\begin{array}{l} C_6H_5\cdot C{:}CH-CO \\ \qquad\quad O\cdot CR'\cdot CR \end{array}.$$

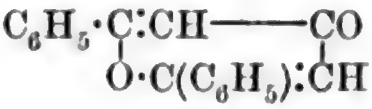
(II.)

It has been found that such a process actually takes place, and that the acetylenic diketones which, no doubt, are first formed condense according to (II) and yield 4-pyrone derivatives. This reaction has been applied to the preparation of 2-phenyl-6-methyl-4-pyrone (III)



$$\begin{array}{l} C_6H_5\cdot C{:}CH\text{———}CO \\ \qquad\quad O\cdot C(CH_3){:}CH \end{array}$$

(III.)



$$\begin{array}{l} C_6H_5\cdot C{:}CH\text{———}CO \\ \qquad\quad O\cdot C(C_6H_5){:}CH \end{array}$$

(IV.)

and 2:6-diphenyl-4-pyrone (IV).

Feist (*Ber.*, 1890, **23**, 3726) showed that the latter compound is formed from dehydrobenzoylacetic acid in the same way as 2:6-dimethyl-4-pyrone is produced from dehydracetic acid. The description of the properties which he gives for this substance differ in one point only from my observations. Feist states that the pyrone derivative dissolves in cold concentrated sulphuric acid, yielding a colourless solution which exhibits a violet fluorescence. This phenomenon was not observed with the specimen described in the present work, but its solutions in sulphuric acid or in boiling concentrated hydrochloric acid are yellow. Oxonium salts are thus produced, which are decomposed by water into the acids and the colourless diphenyl-4-pyrone.

The hydrochloride of 2-phenyl-6-methyl-4-pyrone, however, is not dissociated by water, and this as well as the hydrochloride of the former pyrone derivative, with platinic chloride, yields platinic salts. The fluorescence of the solution of diphenyl-4-pyrone which Feist observed is probably caused by the presence of a trace of another compound formed together with the pyrone on heating dehydrobenzoylacetic acid with concentrated hydrochloric acid. This substance is probably identical with the compound which is produced along with the pyrone by the action of sodium ethoxide on a mixture of ethyl-phenylpropiolate and acetophenone, and which dissolves in cold sulphuric acid to yield a violet solution. It has the composition $C_{25}H_{20}O_3$, and is formed thus:

$$C_6H_5\cdot C\vdots C\cdot CO_2Et + 2C_6H_5\cdot CO\cdot CH_3 = C_{25}H_{20}O_3 + C_2H_6O.$$

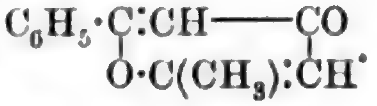
The constitution of the substance may be represented by the formula, $C_6H_5\cdot CH_2\cdot CO\cdot CO\cdot C(CO\cdot C_6H_5){:}C(CH_3)\cdot C_6H_5$. Its formation can easily be explained by assuming that the acetylenic ester is first transformed into the acetylenic-β-diketone, which subsequently reacts with a second molecule of acetophenone, thus:

$$C_6H_5\cdot C\vdots C\cdot CO\cdot CH_2\cdot CO\cdot C_6H_5 = C_6H_5\cdot C\vdots C\cdot CO\cdot C(CO\cdot C_6H_5){:}C(CH_3)\cdot C_6H_5 + H_2O,$$

and that finally the water is added to the acetylenic grouping. Preference is given to this structure, because the other possible formulæ do not allow of an explanation of the fact that the compound is insoluble in either sodium carbonate or potassium hydroxide. The occurrence of this substance in the product of the action of hydrochloric acid on dehydrobenzoylacetic acid can readily be accounted for.

EXPERIMENTAL.

2-Phenyl-6-methyl-4-pyrone,



$$\begin{array}{l} C_6H_5\cdot C{:}CH\text{——}CO \\ \qquad\;\; O\cdot C(CH_3){:}CH \end{array}.$$

This substance is formed on adding to a suspension of dry sodium ethoxide (6·8 grams), in absolute ether, pure acetone (7 grams; prepared from its bisulphite compound), and then gradually ethyl phenylpropiolate (17·4 grams). The mixture, which after a short time sets to a semi-solid, is kept for a day and then treated with water, when the solid dissolves. The ethereal layer, which contains only a very small quantity of a red oil, is separated from the aqueous solution, the latter is mixed with an excess of dilute sulphuric acid, and extracted with ether. On evaporation of the ether, a dark oil is left behind, which contains phenylpropiolic acid besides the pyrone. Without removing the acid by sodium carbonate, the oil may be distilled in a vacuum; at first, carbon dioxide is evolved and phenylacetylene passes over, and then at 220—225° under a pressure of about 14 mm. phenylmethyl-4-pyrone distils as a yellow oil which soon solidifies. The compound is readily soluble in alcohol; on adding water to this solution, an emulsion is produced from which crystals do not separate even on being kept for a day. It is also very soluble in benzene or ether, less so in cold, but readily so in hot, water; it dissolves only sparingly in boiling light petroleum, and, on cooling, crystallises in colourless needles, melting at 87—88°:

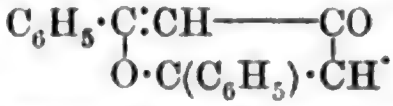
0·2060 gave 0·5835 CO_2 and 0·1005 H_2O. C = 77·25 ; H = 5·42.
$C_{12}H_{10}O_2$ requires C = 77·42 ; H = 5·38 per cent.

2-*Phenyl*-6-*methyl*-4-*pyrone* is very soluble in hydrochloric acid, yielding a hydrochloride which is not dissociated by water; on adding platinic chloride to the solution in hydrochloric acid, yellow needles of the *platinichloride* are formed:

0·2317 gave 0·0572 Pt. Pt = 24·69.
$(C_{12}H_{10}O_2)_2,H_2PtCl_6$ requires Pt = 24·88 per cent.

Action of Acetophenone on Ethyl Phenylpropiolate.

On mixing the suspension of sodium ethoxide (6·8 grams) in dry ether with acetophenone (12 grams) and ethyl phenylpropiolate (17·4 grams), a dark red coloration is produced. The mixture, after being kept for two days, is poured into water, and the ethereal solution separated. This contains the compound $C_{25}H_{20}O_3$, which is described later. The aqueous layer is acidified with dilute sulphuric acid, and extracted with ether. On evaporation of the ether, a brown oil remains behind, which partly solidifies in the course of a few hours. The solid is 2 : 6-diphenyl-4-pyrone,



$$\begin{array}{l} C_6H_5\cdot C{:}CH\text{———}CO \\ \qquad\;\; O\cdot C(C_6H_5)\cdot CH\cdot \end{array}$$

It is freed from the adhering oil by the aid of the pump, and washed with dilute alcohol until it is almost white. The substance is moderately soluble in cold, readily so in boiling, alcohol, and crystallises from dilute alcohol in colourless needles, which on heating behave in the manner stated by Feist (*loc. cit.*); they sinter at about 130°, and melt at 138—139°:

0·2068 gave 0·6220 CO_2 and 0·0933 H_2O. C = 82·02 ; H = 5·01.
0·2023 ,, 0·6096 CO_2 ,, 0·0891 H_2O. C = 82·18 ; H = 4·89.
$C_{17}H_{12}O_2$ requires C = 82·22 ; H = 4·84 per cent.

It has already been mentioned (p. 432) that diphenyl-4-pyrone is soluble in concentrated sulphuric acid and yields a yellow solution. The solution of the substance in hot hydrochloric acid has the same colour as, indeed, have the needles of the hydrochloride which separate on cooling; in the presence of water, the crystals become colourless, owing to the dissociation of the salt into the acid and the pyrone.

On adding platinic chloride to the solution of diphenyl-4-pyrone in hot hydrochloric acid, orange prisms of the *platinichloride* are formed:

0·2625 gave 0·0562 Pt. Pt = 21·41.
$(C_{17}H_{12}O_2)_2,H_2PtCl_6$ requires Pt = 21·47 per cent.

The *compound*, $C_{25}H_{20}O_3$, which is contained in the ethereal solution of the product of the reaction between sodium ethoxide, acetophenone, and ethyl phenylpropiolate, gradually separates before the ether is evaporated, and, on evaporation of the ether, is left behind as a dark solid; on washing with alcohol, it is obtained quite white. The substance is very soluble in chloroform, less so in cold, but readily so in hot, benzene; it dissolves very sparingly in boiling alcohol, and, on cooling, slowly crystallises in colourless prisms, melting at 224°:

0·2055 gave 0·6136 CO_2 and 0·1042 H_2O. C = 81·43; H = 5·64.
0·2003 „ 0·5985 CO_2 „ 0·0984 H_2O. C = 81·53; H = 5·46.
$C_{25}H_{20}O_3$ requires C = 81·52; H = 5·43 per cent.

The substance dissolves in cold concentrated sulphuric acid, yielding a violet solution; it is remarkably stable, and does not dissolve on boiling with hydrochloric acid or dilute potassium hydroxide. On heating with alcoholic potash, it is decomposed, but, besides acetophenone, only a resinous product is formed.

I am engaged in the further study of this compound with the view of examining whether the formula which I have suggested (p. 432) is correct. I propose, also, to investigate on similar lines the behaviour of ketones towards diethyl acetylenedicarboxylate.

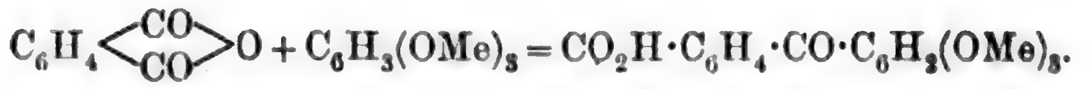
GONVILLE AND CAIUS COLLEGE,
CAMBRIDGE.

XLII.—*Researches on the Anthraquinones.*

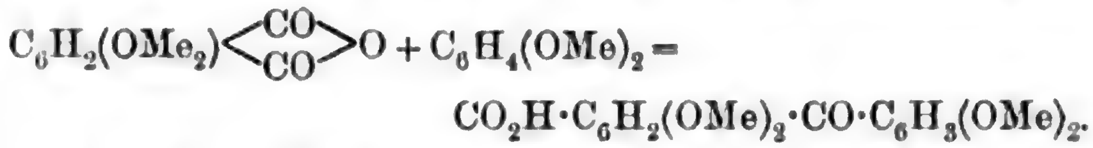
By WILLIAM HENRY BENTLEY and CHARLES WEIZMANN.

IN continuation of the work on the condensation of phthalic acid and its derivatives with the methyl ethers of hydroxybenzenes, attempts have been made to prepare in this manner polyhydroxyanthraquinones. With this object, a study has been made of the condensation products of (I) phthalic anhydride and pyrogallol trimethyl ether; (II) hemipinic anhydride and veratrole, and (III) hemipinic anhydride and pyrogallol trimethyl ether.

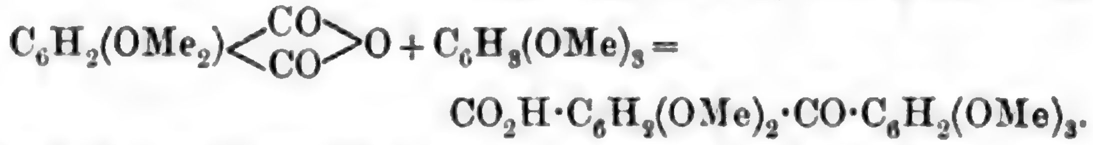
In all three cases, condensation has been effected by means of aluminium chloride in presence of carbon disulphide, the products in the first two reactions being the corresponding benzoylbenzoic acid. In the third reaction, an analysis of the product showed that one methoxy-group had been replaced by the hydroxy-group:



$$\text{(I)}\quad C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O + C_6H_3(OMe)_3 = CO_2H\cdot C_6H_4\cdot CO\cdot C_6H_2(OMe)_3.$$



$$\text{(II)}\quad C_6H_2(OMe_2)\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O + C_6H_4(OMe)_2 = CO_2H\cdot C_6H_2(OMe)_2\cdot CO\cdot C_6H_3(OMe)_2.$$



$$\text{(III)}\quad C_6H_2(OMe_2)\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O + C_6H_3(OMe)_3 = CO_2H\cdot C_6H_2(OMe)_2\cdot CO\cdot C_6H_2(OMe)_3.$$

The yields of acid obtained in these reactions are far from satisfactory, and the purification of the products is somewhat difficult. The pure acids, however, are converted with fairly good yields into anthraquinone derivatives by warming with concentrated sulphuric acid in presence of boric acid, but in all cases the condensation is attended by some de-methylation. Thus, the acids from the reactions (I), (II), and (III) yielded respectively, on treatment with concentrated sulphuric acid, (1) dihydroxymonomethoxyanthraquinone, (2) hydroxytrimethoxyanthraquinone, and (3) trihydroxydimethoxyanthraquinone.

We succeeded, however, in the case of tetramethoxybenzoylbenzoic acid (II) in effecting the condensation without loss of any methoxy-groups by employing phosphoric oxide as the condensing agent, and obtained tetramethoxyanthraquinone by this means.

EXPERIMENTAL.

2′ : 3′ : 4′-(or 3′ : 4′ : 5′-)*Trimethoxy-2-benzoylbenzoic Acid*,*

$CO_2H\cdot C_6H_4\cdot CO\cdot C_6H_2(OMe)_3$.

Aluminium chloride (34 grams) is added in small portions at a time to a mixture of phthalic anhydride (37 grams) and pyrogallol trimethyl ether (42 grams) in carbon disulphide (500 c.c.), and the whole heated on the water-bath for twenty-four hours.

The carbon disulphide is then removed, and the residual mass treated with a large quantity of ice and hydrochloric acid, whereby the acid is obtained as a black oil. After distilling in steam to remove all volatile matter, the oil is washed several times with warm water, then dissolved in sodium carbonate; the solution is boiled with animal charcoal, filtered, and acidified with hydrochloric acid, when the acid is precipitated as an oil which gradually solidifies. The crystals are drained on porous porcelain, and purified by recrystallising from methyl alcohol with the aid of animal charcoal. The yield is very poor, and is not improved by substituting light petroleum (b. p. 120°) for the carbon disulphide:

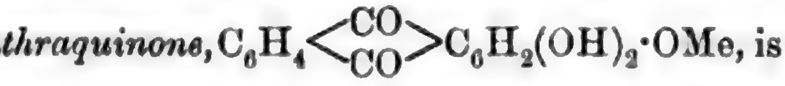
Found, C = 64·7 ; H = 5·4.

$C_{17}H_{16}O_6$ requires C = 64·5 ; H = 5·1 per cent.

---

* For nomenclature see Trans., 1907, **91**, 1630.

2′ : 3′ : 4′-(or 3′ : 4′ : 5′-)*Trimethoxybenzoyl-2-benzoic acid* is a white, crystalline powder, which melts at 169°, and is soluble in the usual organic solvents, but very sparingly so in hot water.

Dihydroxymethoxyanthraquinone,  $C_6H_4{<}\substack{CO\\CO}{>}C_6H_2(OH)_2\cdot OMe$, is produced when the foregoing acid is heated with concentrated sulphuric acid to 140° in the presence of a little boric acid. On pouring the product into ice-water, a brownish-yellow precipitate is obtained, which is filtered and washed with boiling water. After crystallising from acetic acid, it is obtained in bright orange-coloured flakes melting at 235—236°:

Found, $C = 66{\cdot}1$; $H = 4{\cdot}2$.

$C_{15}H_{10}O_5$ requires $C = 66{\cdot}6$; $H = 3{\cdot}7$ per cent.

The presence of one methoxyl group was confirmed by Zeisel's method:

Found, $OMe = 11{\cdot}7$.

$C_{14}H_7O_4\cdot OMe$ requires $OMe = 11{\cdot}5$ per cent.

Tetramethoxy-2-benzoylbenzoic Acid,
$CO_2H\cdot C_6H_2(OMe)_2\cdot CO\cdot C_6H_3(OMe)_2$.

This acid is prepared from hemipinic anhydride (50 grams), veratrole (30 grams), and aluminium chloride (50 grams) exactly in the same manner as the preceding acid. It separates from methyl alcohol as a white powder melting at 193—194°:

0·1328 gave 0·3030 CO_2 and 0·0647 H_2O. $C = 62{\cdot}2$; $H = 5{\cdot}4$.

$C_{18}H_{18}O_7$ requires $C = 62{\cdot}4$; $H = 5{\cdot}2$ per cent.

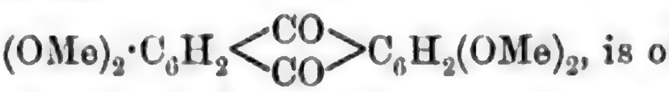
This acid dissolves in sodium carbonate to a colourless solution.

It readily condenses in concentrated sulphuric acid; at 60°, the product obtained is a *monohydroxytrimethoxyanthraquinone*, which crystallises from acetic acid in yellow needles melting at 226°:

0·1128 gave 0·2695 CO_2 and 0·0458 H_2O. $C = 65{\cdot}16$; $H = 4{\cdot}51$.

$C_{17}H_{14}O_6$ requires $C = 64{\cdot}97$; $H = 4{\cdot}46$ per cent.

The substance dissolves in sulphuric acid with a violet-red, and in alcoholic potash with a bright red, colour. It is sparingly soluble in alcohol, more readily so in acetic acid.

Tetramethoxyanthraquinone,  $(OMe)_2\cdot C_6H_2{<}\substack{CO\\CO}{>}C_6H_2(OMe)_2$, is obtained when tetramethoxy-2-benzoylbenzoic acid is mixed with phosphoric oxide, and gently heated until fusion occurs. The product is poured into water, and the yellow solid washed with hot dilute sodium hydroxide and afterwards with hot water and crystallised from acetic acid, from which it separates in yellow needles melting at 239°:

0·1171 gave 0·2824 CO_2 and 0·0544 H_2O. C = 65·77; H = 5·16.
$C_{18}H_{16}O_6$ requires C = 65·85; H = 4·88 per cent.

The substance is sparingly soluble in alcohol; its alcoholic solution gives no coloration with potassium hydroxide. It is soluble in concentrated sulphuric acid with a violet-red colour, but does not dissolve in aqueous potassium hydroxide.

Hydroxytetramethoxy-2-benzoylbenzoic Acid,

$CO_2H{\cdot}C_6H_2(OMe)_2{\cdot}CO{\cdot}C_6H_2(OMe)_2{\cdot}OH$ or
$CO_2H{\cdot}C_6H_2(OH)(OMe){\cdot}CO{\cdot}C_6H_2(OMe)_3$.

As stated in the introduction, the condensation of pyrogallol trimethyl ether with hemipinic anhydride takes place with the loss of one methoxy-group. The acid, which is isolated in the usual way, crystallises from methyl alcohol in minute prisms, which melt indefinitely at 190°:

0·1290 gave 0·2818 CO_2 and 0·0582 H_2O. C = 59·58; H = 5·01.
$C_{18}H_{18}O_8$ requires C = 59·66; H = 4·97 per cent.

Hydroxytetramethoxy-2-benzoylbenzoic acid dissolves in sodium carbonate, forming a yellow solution. It gives a red solution with concentrated sulphuric acid, which, on heating to about 140°, changes to violet, due to the formation of *trihydroxydimethoxyanthraquinone*: this is purified by recrystallisation from acetic acid, from which it separates in red needles melting at 230°:

0·1115 gave 0·2476 CO_2 and 0·0401 H_2O. C = 60·56; H = 3·99.
$C_{16}H_{12}O_7$ requires C = 60·76; H = 3·79 per cent.

The substance is soluble in potassium hydroxide or sodium carbonate, forming reddish-violet solutions, and its solution in concentrated sulphuric acid is deep violet. It is a mordant dye-stuff.

Our best thanks are due to Messrs. H. Watson and P. S. MacMahon for assistance in this work.

UNIVERSITY,
MANCHESTER.

XLIII.—*Organic Derivatives of Silicon. Part V. Benzylethylsilicone, Dibenzylsilicone, and other Benzyl and Benzylethyl Derivatives of Silicane.*

By ROBERT ROBISON, B.Sc., and FREDERIC STANLEY KIPPING.

THE silicones, those derivatives of silicon analogous to the ketones in structure, have not yet been very carefully studied, and, in fact, only a few compounds of this type have hitherto been prepared.

The simplest known representative, diethylsilicone, Et_2SiO, was obtained long ago by Friedel (*Ann. chim. phys.*, 1866, [iv], **9**, 5); diphenylsilicone, Ph_2SiO, has been described by Dilthey (*Ber.*, 1905, **38**, 4132), and phenylethylsilicone, PhEtSiO, was prepared by one of us a short time ago (Trans., 1907, **91**, 218).

In the course of some recent experiments (Kipping, Trans., 1907, **91**, 720), it was found that benzylethylsilicon dichloride could be easily obtained in a pure state; as this compound is decomposed by water, giving benzylethylsilicone, BzEtSiO, we have studied the behaviour of this silicone in order to ascertain whether it shows any similarity to the corresponding ketone. We may say at once that it does not; benzyl ethyl ketone boils at 226° under atmospheric pressure; benzylethylsilicone at 305—315° under a pressure of 22 mm. This very high boiling point of the silicone doubtless indicates molecular complexity, and the results of ebullioscopic experiments bear out this indication, the values obtained in acetic acid and in acetone pointing to the termolecular formula $(BzEtSiO)_3$. In this respect, benzylethylsilicone resembles diphenylsilicone (Dilthey, *loc. cit.*); dibenzylsilicone, which is described in this paper (p. 452), is also represented by the molecular formula $(Bz_2SiO)_3$, and, judging from its high boiling point (above 360°), diethylsilicone has an analogous molecular complexity. It would seem, therefore, that silicones, as a class, differ from the ketones in readily forming comparatively stable molecular aggregates, but whether the latter are to be regarded as composed of loosely associated, or of chemically united, molecules we have as yet no satisfactory evidence before us.

This association, polymerisation, or union of the simple silicone molecules is probably one of the reasons, but not the only one, why in other respects also the silicones show no relationship with the ketones; thus we find that benyzlethylsilicone does not undergo change when it is treated with certain reagents which reduce ketones; we also find that the silicone does not react with hydroxylamine or with phenylhydrazine when treated with these reagents in the ordinary way. In both these cases, it is possible to account for the result on the assumption that the grouping Si:O of the simple silicone does not exist in the associated molecule, but, since we know from previous experiments (Kipping, *loc. cit.*) that the union between nitrogen and silicon is dissolved in presence of water, the non-formation of an oxime or hydrazone may not be in any way determined by the association of the silicone.

Having found that benzylethylsilicone did not react with the ordinary ketonic reagents, we attempted to prepare its sulphonic derivative. As a number of derivatives of silicane which contain a benzyl group undergo sulphonation very readily, whereas those containing phenyl or alkyl groups do not, it seemed extremely probable that in all the former the sulphonic group displaced hydrogen of the benzyl nucleus; this conclusion was confirmed by the fact that benzylethylsilicone could be sulphonated without difficulty, but, unfortunately, the salts of the acid, which is produced as the main product, did not crystallise well.

In the preparation of the benzylethylsilicon dichloride which was required for these and for other experiments, a considerable proportion of an oily by-product was invariably obtained (Kipping, *loc. cit.*, p. 721); having collected a large quantity of this oil from different preparations, it seemed worth while to try to isolate the dibenzylethyl silicyl chloride, of which we thought the product was mainly composed. After working at this by-product for some time, we realised that it was a far more complex mixture than we had supposed, and ultimately we found that it contained, in addition to dibenzyl and some stilbene, dibenzylethylsilicyl chloride, dibenzylsilicon dichloride, tribenzylsilicyl chloride, and other compounds which were not identified.

The occurrence in this mixture of dibenzylsilicon dichloride and of tribenzylsilicyl chloride is possibly due to the presence of silicon tetrachloride in the ethylsilicon trichloride used for the preparation of the benzylethyl derivative; as, however, ethylsilicon trichloride boils at 100°, and all the preparations which we used had been repeatedly fractionated, employing a rod and disk column, it hardly seems likely that they could have contained silicon tetrachloride (b. p. 58°), at any rate, in quantity sufficient to yield any appreciable proportion of its dibenzyl and tribenzyl derivatives. It seems more likely, therefore, that the observed formation of these compounds is due to the displacement of the ethyl by a benzyl group during the treatment of the ethylsilicon trichloride with magnesium benzyl chloride; such a reaction is not inherently improbable, and, for different reasons altogether, it has been already suggested that a change of this kind may occur (Kipping, *loc. cit.*, p. 730).

On decomposing with water some of the impure dibenzylsilicon dichloride isolated from the product mentioned above, we obtained a crystalline substance melting at 101°, and the results of the examination of this compound led us to conclude that it was a hydrol of the formula $Bz_2Si(OH)_2$. The only reason for hesitation in coming to this conclusion was that Dilthey (*loc. cit.*) had recently described under the name dibenzylsilicol, a compound to which he assigned the formula $Bz_2Si(OH)_2$, and an approximate melting point of 76°. He obtained this compound by treating silicon tetrachloride with three molecular proportions of magnesium benzyl chloride, decomposing the product with water, and then crystallising from a mixture of benzene and light petroleum, rejecting the portions melting above 76° which contained tribenzylsilicol. As such a method could hardly yield a pure substance, as, in fact, seemed to be admitted by Dilthey himself, we thought it probable that his preparation, the melting point of which had been *lowered* to 76°, was a mixture of the hydrol and tribenzylsilicol. But as Dilthey's numerous analyses all gave results agreeing with those required for the hydrol alone, we thought it advisable to investigate the matter further.

Having prepared a considerable quantity of pure dibenzylsilicon dichloride, which crystallises in magnificent transparent prisms, some of this preparation was decomposed with water; the product after recrystallisation melted at 101°, and was identical with the supposed hydrol previously obtained. Further evidence of the nature of this product was afforded by its behaviour when heated; when kept at 110° for six hours, it was converted into dibenzylsilicone, a crystalline compound melting at 98°, and quite different from the hydrol in outward properties. At this stage, we were naturally very doubtful as to the purity of Dilthey's "dibenzylsilicol" melting at 76°, but, on attempting to prepare a further quantity of ketone by heating the hydrol (m. p. 101°) at 110°, we obtained instead a substance which was not dibenzylsilicone, and which, after repeated recrystallisation, melted at about 75°, but not sharply; this compound formed well-defined, transparent prisms, had the appearance of a pure substance, and on analysis gave results agreeing with those required by a hydrol of the formula $Bz_2Si(OH)_2$. Later, this hydrol melting at 75° was obtained directly in place of the hydrol melting at 101° by decomposing dibenzylsilicon dichloride with water, and crystallising the product from a mixture of ether and light petroleum. It seems very probable that the substance melting at 75° is identical with Dilthey's dibenzylsilicol (m. p. 76°); in any case, since our experiments show that both this and the compound melting at 101° have the molecular formula $Bz_2Si(OH)_2$, we are forced to the conclusion that the two hydrols are isomeric. Details of the experimental evidence leading to this conclusion are given, but it may be stated here that, in addition to the analyses and molecular weight determinations, it is shown that both the hydrols may be converted into dibenzylsilicone under suitable conditions.

In spite of their isomerism, the two hydrols, which we distinguish as α (m. p. 101°) and β (m. p. 75°), differ very greatly in outward characteristics, and also, in one noteworthy respect, in chemical properties; whereas the α-compound is practically unchanged in a dry vacuum, the β-hydrol becomes oily, owing to loss of the elements of water; further, although we have never succeeded in regenerating the α-hydrol after it has once lost the elements of water, the β-hydrol is readily formed again on exposing its oily decomposition product to moist air. This difference seemed to indicate a possible explanation of the observed isomerism; the α-hydrol might be regarded as a compound of the structure $Bz_2Si\begin{smallmatrix}\diagup OH\\ \diagdown OH\end{smallmatrix}$, and the β-isomeride as unimolecular dibenzylsilicone crystallised with one molecule of water; the results of our cryoscopic experiments, however, do not lend any support to this view, which, after all, is barely susceptible of clear definition, and up to the present, unless we consider the possibility that the β-hydrol may have the constitution $Bz_2Si{:}O{:}O\begin{smallmatrix}\diagup H\\ \diagdown H\end{smallmatrix}$, no other explanation has suggested itself. That examples of isomerism among derivatives of silicon containing oxygen, without parallel in the case of corresponding carbon derivatives, will be no uncommon occurrence, seems to be foreshadowed by these results, as well as by Dilthey's observations on the probable existence of isomeric termolecular diphenylsilicones (*loc. cit.*).

There are several points in connexion with these hydrols which have not yet been very satisfactorily settled, for example, the fact that neither compound gives pure ketone when it is heated at 100°; it is hoped that this and other matters of interest will be cleared up later, the publication of our results in their present state being necessitated by unavoidable circumstances.

EXPERIMENTAL.

Benzylethylsilicone, BzEtSiO.

The benzylethylsilicon dichloride employed in this investigation was prepared by the method recently described (Kipping, Trans., 1907, **91**, 720). As preliminary experiments showed that the silicone obtained from it would not be easily purified by distillation, the dichloride itself was very carefully fractionated, and the portion boiling constantly at 169° (100 mm.) collected separately. Analyses of these preparations were made by decomposing a weighed quantity with alcoholic silver nitrate solution in the manner previously described (*loc. cit.*, p. 217):

Preparation A : 0·6376 gave 0·8188 AgCl. Cl = 31·7.
Preparation B : 0·4736 „ 0·6134 AgCl. Cl = 32·0.
$C_9H_{12}Cl_2Si$ requires Cl = 32·3 per cent.

The fractions of benzylethylsilicon dichloride boiling just above 169° contained only a little dibenzyl as impurity; in later experiments, the silicone was prepared from some of these, and the dibenzyl separated by distillation in steam; the product thus obtained was scarcely less pure than that prepared from the fractions boiling at 169°.

Benzylethylsilicon dichloride is rapidly decomposed by water, and a considerable rise in temperature occurs. The oily product was extracted with pure ether, the solution washed with water, dried, and evaporated. The residue was a colourless, viscous oil; it was left for some time in a vacuum over sulphuric acid, and then analysed with the following results:

0·3294 gave 0·1218 SiO_2. Si = 17·3.
0·1959 „ 0·4668 CO_2 and 0·1291 H_2O. C = 65·0; H = 7·3.
$C_9H_{12}OSi$ requires Si = 17·3; C = 65·7; H = 7·4 per cent.

Benzylethylsilicone is insoluble in water, but miscible with ether, light petroleum, and other organic solvents.

When the silicone is distilled under reduced pressure (22 mm.), 70—80 per cent. of the whole passes over between 305° and 315°, but there then remains a dark-coloured residue which does not distil at 360°; on redistilling the portion collected from 305—315°, 70 to 80 per cent. again passes over between the same temperatures as before, and again there remains a dark-coloured residue of much higher boiling point. Water seems to be formed in small quantity, and on opening the flask there is generally a very strong odour of benzaldehyde. The distillate is nearly colourless, and on analysis proves to be the unchanged silicone, whereas the residue, which is very viscous, gives a higher percentage of silicon.

The following results were obtained with the distilled benzylethylsilicone:

0·3508 gave 0·1292 SiO_2. Si = 17·2.
0·1582 „ 0·3815 CO_2 and 0·1060 H_2O. C = 65·8; H = 7·4.
$C_9H_{12}OSi$ requires Si = 17·3; C = 65·7; H = 7·4 per cent.

Since the boiling point of benzylethylsilicone is so much higher than that of the corresponding carbon compound, benzyl ethyl ketone (b. p. 226°/760 mm.), it seemed very probable that the molecule of the former was highly associated and not represented by the simple formula BzEtSiO. This view was confirmed by molecular weight determinations made by the ebullioscopic method. Both the undistilled and the distilled silicone were used, but the two preparations gave similar results:

Undistilled Benzylethylsilicone.

Solvent.	Weight of substance in grams.	Weight of solvent in grams.	Percentage concentration.	Δ.	Mol. wt.
Acetic acid	0·374	15·4	2·3	0·150°	429
	0·761	15·4	4·7	0·290	441
	1·104	15·4	6·7	0·368	493
Acetone	0·248	10·0	2·4	0·093	445
	0·526	10·0	5·0	0·193	455
	0·896	10 0	8·2	0·323	463

Distilled Benzylethylsilicone.

Solvent.	Weight of substance in grams.	Weight of solvent in grams.	Percentage concentration.	Δ.	Mol. wt.
Acetic acid	0·311	10·5	2·9	0·180°	416
	0·673	10·5	6·0	0·356	454
	1·016	10·5	8·8	0·510	480
	1·356	10·5	11·4	0·666	490

As the formula BzEtSiO requires a molecular weight of 164·5, it seems clear that the liquid silicone is a compound of complex molecules $(BzEtSiO)_3$.

Diphenylsilicone, according to the observations of Dilthey (*Ber.*, 1905, **38**, 4134), exists in two modifications, namely, in a gelatinous form, melting at 105—110°, and in a crystalline form, melting at 188°; the molecular weights of these two substances were determined by him in benzene solution, and, whereas in the case of the latter the results indicated a termolecular association $(Ph_2SiO)_3$, in the former they were apparently not conclusive, although pointing to a similar complexity. We have not observed the formation of any solid form of benzylethylsilicone; the substance has been kept for several months in a desiccator over sulphuric acid, it has been kept for a long time at 0°, and also treated with a drop of acetic anhydride, a reagent which converts gelatinous diphenylsilicone into the crystalline form, but without any obvious result.

The very viscid, brown residue which remains on distilling benzylethylsilicone under reduced pressure does not seem to be simply another form of the silicone, but a condensation product; as it could not be purified, we merely determined the silicon in the crude substance and carried out some molecular weight determinations with the following results:

0·3049 gave 0·1200 SiO_2. Si = 18·4.

Solvent.	Weight of substance in grams.	Weight of solvent in grams.	Percentage con- centration.	Δ.	Mol. wt.
Acetic acid	0·397	10·4	3·7	0·155°	622
	0·770	10·4	6·9	0·245	764
	1·037	10·4	9·1	0·355	711
Acetone	0·423	10·0	4·1	0·103	686

Behaviour of Benzylethylsilicone towards Ketonic Reagents.

Phenylhydrazine seems to have no action on benzylethylsilicone; equal quantities of the base and the silicone were warmed together at 100° for two hours, and the two substances were also heated together at 100° for two hours in glacial acetic acid solution. In each case, after shaking the ethereal solution of the silicon compound with very dilute hydrochloric acid and evaporating, the resulting oil was free from nitrogen.

Hydroxylamine also seems to have no action on the silicone in alcoholic potash solution.

Attempts were made to prepare derivatives of the silicone by treating benzylethylsilicon dichloride with bases such as phenylhydrazine and *p*-toluidine, but a definite compound was not isolated in either case; even if the expected interaction occurred, the product was decomposed by the acid or water employed in removing the excess of the base, and was free from nitrogen.

Benzylethylsilicone is not reduced by sodium and alcohol. A sample which had been thus treated with a large excess of the theoretical quantity of sodium was as viscous as before, and gave no effervescence with sodium. It was next dissolved in ether, the solution poured on to a concentrated solution of potassium hydroxide, and, finally, sodium added in small quantities at a time, using a large excess. The product showed no signs of having been reduced, and on analysis gave results which showed it to be the unchanged silicone.

0·1981 gave 0·4693 CO_2 and 0·1370 H_2O. C = 64·7; H = 7·7.

$C_9H_{12}OSi$ requires C = 65·7; H = 7·4 per cent.

$C_9H_{14}OSi$,, C = 64·8; H = 8·5 ,, ,,

Although the above experiments show that benzylethylsilicone is relatively a very inert substance, a vigorous reaction takes place when it is mixed with an ethereal solution of magnesium ethyl bromide; unfortunately, we have not yet been able to investigate the product.

Sulphobenzylethylsilicone, $EtSiO{\cdot}CH_2{\cdot}C_6H_4{\cdot}SO_3H$.

When the silicone is heated with ordinary sulphuric acid (2 vols.) at 100° for about two hours, it passes into solution and no precipitate is produced on subsequently diluting with water. The aqueous solution, having been neutralised with barium carbonate, filtered, and evaporated, gives the *barium* salt of a sulphonic derivative of silicon as a colourless, but not visibly crystalline, solid residue. This substance is sparingly soluble in cold, but readily so in hot, water, except that there is always a slight residue which does not dissolve; it is insoluble in alcohol. The crude product was separated into two parts by fractional crystallisation from water, and each portion was analysed by heating a weighed quantity with distilled sulphuric acid.

Less Soluble Portion:

0·2570 gave 0·1432 residue $(SiO_2 + BaSO_4) = 55·7$.

More Soluble Portion:

0·2894 gave 0·1580 residue $(SiO_2 + BaSO_4) = 54·6$.
$(EtSiO·CH_2·C_6H_4·SO_3)_2Ba$ requires $(SiO_2 + BaSO_4) = 56·7$ per cent.

A little of the salt was decomposed with the exact amount of sulphuric acid, the solution filtered, and the filtrate evaporated. The sulphonic acid so obtained was a colourless, viscous liquid, and gave a residue of silica on ignition.

These experiments having indicated that the sulphonation product was a monosulphonic derivative of benzylethylsilicone, a portion of the barium salt was treated with excess of ammonium carbonate solution; after filtering, evaporating, and heating until all the ammonium carbonate was expelled, there remained a colourless, very hygroscopic *ammonium* salt, which was also freely soluble in methyl and ethyl alcohols. A solution of this salt was treated with solutions of silver nitrate, lead acetate, calcium chloride, and a number of other metallic salts, but no precipitate was obtained; solutions of *p*-toluidine, quinine, cinchonine, and cinchonidine hydrochlorides gave colourless solid precipitates, but all attempts to obtain these compounds in a well-crystallised state were unsuccessful.

The *quinine* salt, after drying at 100°, melted at 180—200°; although it did not seem to be at all hygroscopic, mere contact with a little methyl alcohol, ethyl alcohol, acetone, ethyl acetate, or mixtures of these solvents converted it into an oil. Having failed to obtain a crystallised derivative, we returned to the barium salt; the original preparation was fractionally precipitated from its aqueous solution by the addition of alcohol; in this way, we finally obtained from it a relatively very small quantity of a salt almost insoluble in warm water, but soluble in presence of the other portion of the original preparation. This sparingly soluble salt was boiled with excess of ammonium carbonate solution, and the filtrate was heated until all ammonium carbonate was expelled. The residue was then dissolved in dilute alcohol, and the solution allowed to evaporate spontaneously; flat, colourless prisms were then deposited, but only a small quantity of these well-defined crystals was obtained. As this salt was not analysed, its composition cannot be stated with certainty, but, as it contained silicon and gave ammonia when heated with potash, it is very probable that it was a pure ammonium salt of benzylethylsiliconesulphonic acid.

The readily soluble portion of the barium salt was dried at 100° until constant and then analysed:

0·3074 gave 0·1726 residue ($SiO_2 + BaSO_4$) = 56·1.

$C_{18}H_{22}O_8S_2BaSi_2$ requires ($SiO_2 + BaSO_4$) = 56·7 per cent.

This salt was also converted into the ammonium salt, which, however, did not crystallise well; it was a colourless, hygroscopic substance, only moderately soluble in alcohol.

From the above experiments, we conclude that in the sulphonation of the silicone two isomeric acids (probably the ortho- and para-compounds) are formed.

By-products from the Preparation of Benzylethylsilicon Dichloride.

The product of the interaction of ethylsilicon trichloride and magnesium benzyl chloride is a complex mixture; after separating the benzylethylsilicon dichloride, which is contained in the fraction collected below 200° under a pressure of 100 mm., there remains a considerable quantity of a rather viscid, brown, fuming liquid. Having accumulated a considerable quantity of this by-product from a number of different experiments, we submitted the whole to systematic fractional distillation under reduced pressure (100 mm.) in a long-necked flask provided with a rod and disk column. The fractions of lowest boiling point thus obtained solidified on cooling, and consisted principally of dibenzyl, which accumulated in the portions distilling from about 190° to 244°; those portions distilling between 220° and 244° also contained a little stilbene.

A considerable quantity of a fuming liquid, boiling almost constantly at 244—248° (100 mm.), was the next fraction collected; this product is described below. Above 248°, the thermometer rose continuously and fairly rapidly to about 300°, and this portion of the distillate yielded no definite product. From 300° to 360°, there passed over a rather thick, yellow liquid containing tribenzylsilicyl chloride, the isolation of which is also described later (p. 450).

a-Dibenzylsilicol, $Bz_2Si(OH)_2$.

The fraction boiling at 244—248° (100 mm.) seemed to be a fairly pure compound, and, from its boiling point, was thought to consist of dibenzylethylsilicyl chloride, $Bz_2EtSiCl$. A sample was analysed by decomposing it with aqueous ammonia, evaporating until neutral, and then titrating with silver nitrate solution (1 c.c. = 0·00178 Cl):

0·1940 required 19·5 c.c. Cl = 17·9.
0·2005 „ 20·1 c.c. Cl = 17·8.

$C_{16}H_{19}ClSi$ requires Cl = 13·0; $C_{14}H_{14}Cl_2Si$ requires Cl = 25·2 per cent.

These results showed that the liquid contained a large proportion of some substance far richer in chlorine than dibenzylethylsilicyl chloride, and the only compound which fulfilled this condition and the presence of which seemed possible was dibenzylsilicon dichloride; as this substance would probably have a boiling point approximately the same as that of dibenzylethylsilicyl chloride, and, if present, could hardly be separated by further fractional distillation, the whole of the chloride, was decomposed with water and the resulting oil extracted with ether. On evaporation, there was obtained a colourless solid substance, which, however, contained some oil; this latter was removed by washing with light petroleum, but attempts to purify the solid substance further by recrystallisation from benzene, a mixture of light petroleum and ether, or light petroleum and benzene, were only partly successful; each time the substance was dissolved, decomposition seemed to take place, and the quantity of solid rapidly diminished. At last, however, by the spontaneous evaporation of an alcoholic solution, a small quantity of substance was obtained in long, asbestos-like prisms, melting at 101°. This compound was readily soluble in ether, benzene, or alcohol, but almost insoluble in light petroleum and insoluble in water. When kept at a temperature slightly below its melting point for a short time, it liquefied; on cooling a little, crystals reappeared, but the substance did not solidify entirely until the temperature fell to 50°. Its behaviour resembled that of a solid crystallising from its saturated solution, but with this modification, that as long as the temperature was maintained above 50° the solid changed into the liquid phase at an appreciable rate. After having been heated at about 160°, the substance remained entirely liquid at 0°.

An analysis of the crystals, melting at 101°, which had been dried over sulphuric acid gave the following results:

0·1974 gave 0·4978 CO_2 and 0·1200 H_2O. C = 68·8; H = 6·7.

$C_{14}H_{16}O_2Si$ requires C = 68·7; H = 6·5 per cent.

From its behaviour during the combustion, the boiling point of this substance, or rather that of the liquid into which it changes, must be very high, probably above 400°.

The method of formation of this compound, its behaviour on solution and when heated, and the analytical results, led us to conclude that it was dibenzylsilicol, $Bz_2Si(OH)_2$; such a compound when heated would doubtless lose water, giving the silicone, and the latter would then probably pass into a substance of very high boiling point, represented by the molecular formula $(Bz_2SiO)_3$, analogous to the polymeric modification of benzylethylsilicone (p. 444). The further investigation of this compound is described later (p. 452).

Dibenzylethylsilicol, $Bz_2EtSi{\cdot}OH$.

The oily portion of the product obtained by treating the chloride with water and separated from the dibenzylsilicol by filtration (together with the oil obtained from the decomposition of the hydrol during recrystallisation) was fractionally distilled under a pressure of 25 mm. The thermometer rose immediately to about 205°, and between this temperature and 215° about 40 per cent. of the whole liquid distilled; the thermometer then rose again very rapidly to about 360°, at which temperature heating was discontinued; the undistilled residue formed about 50 per cent. of the whole; it was not further examined, but it seems very probable that it consisted principally of the polymerised dibenzylsilicone, $(Bz_2SiO)_3$, formed by the decomposition of the hydrol already described. The fraction collected between 205° and 215° was redistilled under the same pressure (25 mm.) as before, and the portion boiling at 207—212° collected separately. When kept for some time in a freezing mixture, this liquid deposited a small quantity of a crystalline substance which was ultimately found to be a mixture of stilbene and a compound containing silicon and melting at 54°. The stilbene was identified by its melting point, 120—121°, and by converting it into its well-crystallised dibromide (α), which melted at 233°; its presence cannot be accounted for. The crystalline silicon compound (m. p. 54°) is described later. After separating the crystalline deposit, the oil was analysed:

0·7610 gave 0·1627 SiO_2. Si = 10·0.
0·3624 ,, 0·0775 SiO_2. Si = 10·1.
0·2517 ,, 0·6967 CO_2 and 0·1800 H_2O. C = 75·5; H = 7·9.
$C_{16}H_{20}OSi$ requires Si = 10·9; C = 75·0; H = 7·8 per cent.

The results of the combustion agree satisfactorily with those required for dibenzylethylsilicol, and in spite of the discordance between the theoretical and experimental values for the percentage of silicon we are of the opinion that this preparation was a moderately pure sample of the silicol; this conclusion is rendered extremely probable by the facts described below.

Dibenzylethylsilicyl Oxide, $(Bz_2EtSi)_2O$.

The preparation of dibenzylethylsilicol just described was left over sulphuric acid in a vacuum previous to making another analysis; it was then observed that the oil had deposited crystals, which melted at 54°, like those previously separated. An analysis of the remaining oil also showed that the percentage of carbon was now much higher than before, an indication that some decomposition, probably the elimination of water, had occurred:

0·1842 gave 0·5204 CO_2 and 0·1336 H_2O. C = 77·0; H = 8·0.

After some time, practically the whole of the oil became changed into these crystals, which were purified by recrystallisation from alcohol. They then melted sharply at 55°, and on analysis gave results agreeing with those required for the oxide of dibenzylethylsilicol, $(Bz_2EtSi)_2O$, thus confirming the constitution of the oil from which they were derived:

0·1976 gave 0·5617 CO_2 and 0·1399 H_2O. C = 77·5; H = 7·9.
0·1717 „ 0·4870 CO_2 „ 0·1192 H_2O. C = 77·4; H = 7·7.
$C_{32}H_{38}OSi_2$ requires C = 77·6; H = 7·7 per cent.

A molecular weight determination was also made by the ebullioscopic method in acetone solution with the following result:

0·387 in 10·2 acetone gave $\Delta t - 0·135$. Mol. wt. = 452.

As the calculated molecular weight for the silicol is 257 and for the oxide 495, there does not seem to be much doubt as to the nature of the compound. *Dibenzylethylsilicyl oxide* crystallises in glistening plates, is moderately soluble in warm alcohol, and readily so in ether. A little of the substance was boiled with potassium hydroxide for a short time to try to reconvert it into the silicol, but its melting point was found to be unchanged by this treatment.

Tribenzylsilicyl Chloride, Bz_3SiCl.

The fraction of the original by-product (p. 447) collected from 300° to 360° (100 mm.) slowly deposited long needles. These were quickly separated by filtration, and spread on porous earthenware in a desiccator. After recrystallising twice from light petroleum, they were obtained in slender, colourless prisms, moderately soluble in hot light petroleum, readily so in ether, but very sparingly so in cold light petroleum. The compound melted at 141°, and, although it did not fume perceptibly in the air, it was readily decomposed by water;

a chlorine estimation was made by the volumetric method (1 c.c. $AgNO_3 = 0·00178$ Cl):

0·2735 required 16·2 c.c. $AgNO_3$; Cl = 10·5.

$C_{21}H_{21}ClSi$ requires Cl = 10·5 per cent.

Tribenzylsilicol, $SiBz_3·OH$.

The chloride just described was warmed with moist alcohol, and the product recrystallised from light petroleum; it separated in colourless needles, melting sharply at 104°, and was readily soluble in ether, but only moderately so in light petroleum:

0·1024 gave 0·2974 CO_2 and 0·0665 H_2O. C = 79·2; H = 7·2.

$C_{21}H_{22}OSi$ requires C = 79·1; H = 7·0 per cent.

Tribenzylsilicol has recently been described by Dilthey (*loc. cit.*), who gives its melting point as 106°.

Dibenzylsilicon Dichloride, Bz_2SiCl_2.

In order to confirm some of the results of the experiments described above, a quantity of dibenzylsilicon dichloride was prepared from silicon tetrachloride. To 1 molecule of the latter, $2\frac{2}{5}$ molecules of magnesium benzyl chloride were slowly added with vigorous cooling and stirring. The whole was allowed to stand overnight, the ether then evaporated, and the residue heated at 100° for three hours. It was then extracted with ether in the apparatus already described (Kipping, Trans., 1907, **91**, 216). After distilling off the ether, the residual oil was fractionally distilled under a pressure of 100 mm., using a long-necked flask with rod and disk column. A small quantity passed over below 200°, and then a large fraction between 200° and 240° which became solid on cooling, and consisted of dibenzyl; from about 240°, the thermometer rose very slowly, and a large proportion of the whole distilled below 250°; above 250°, the thermometer rose more rapidly to 360°, but there still remained a considerable residue of viscid, brown oil which did not distil at 360°. The fraction 241—250° was distilled twice more, and, finally, the portion boiling between 241—245° was collected separately; after having been kept in a closed vessel for some time, the colourless oil solidified completely. It was then recrystallised from light petroleum, from which it was obtained in magnificent, colourless prisms; these were moderately soluble in light petroleum, and melted at 50—52°; they fumed somewhat in the air, and, when previously reduced to a powder, were readily decomposed by water; otherwise a thin film of the insoluble decomposition product was formed at the surface and prevented further action of the water. An analysis of these crystals was carried out volumetrically (1 c.c. $AgNO_3 = 0{\cdot}00178$ Cl):

0·1385 required 19·9 c.c. $AgNO_3$; Cl = 25·5.
0·2407 „ 34·4 c.c. $AgNO_3$; Cl = 25·4.
$C_{14}H_{14}Cl_2Si$ requires Cl = 25·2 per cent.

This pure dichloride was decomposed by dissolving it in ether and shaking the solution with water until free from hydrochloric acid. The substance obtained melted at 101°, softening slightly at 98°, and was identical with the *a*-dibenzylsilicol previously described (p. 448), as proved by the following analyses:

0·4200 gave 0·1058 SiO_2. Si = 11·8.
0·1960 „ 0·4953 CO_2 and 0·1206 H_2O. C = 68·9; H = 6·8.
0·1172 „ 0·2963 CO_2 „ 0·0711 H_2O. C = 68·9; H = 6·8.
$C_{14}H_{16}O_2Si$ requires Si = 11·6; C = 68·7; H = 6·5 per cent.

Molecular weight determinations were carried out by the cryoscopic method with the following results:

0·184 in 18·3 acetic acid gave Δt – 0·155°. Mol. wt. = 251.
0·347 „ 18·3 „ „ „ „ 0·295°. „ „ = 249.
0·625 „ 18·0 „ „ „ „ 0·570°. „ „ = 236.
0·838 „ 19·2 „ „ „ „ 0·730°. „ „ = 232.
$C_{14}H_{16}O_2Si$ requires Mol. wt. = 244·6.

Dibenzylsilicone, Bz_2SiO.

The substance just referred to as *a*-dibenzylsilicol, and prepared by decomposing pure dibenzylsilicon dichloride with water, was certainly not identical with the substance (m. p. 76°) obtained by Dilthey (*loc. cit.*), and to which he assigned the formula $Bz_2Si(OH)_2$.

In order to obtain some further confirmation of the nature of our compound, we heated a small quantity of it at 110° for six hours with the object of converting it into the corresponding ketone. The oily product was then dissolved in a mixture of alcohol and ether, from which it separated in colourless prisms, and after recrystallisation from light petroleum these melted at 98°. The compound was readily soluble in ether, and moderately so in alcohol or light petroleum. A preparation was analysed with the following results:

0·1707 gave 0·4653 CO_2 and 0·1002 H_2O. C = 74·3; H = 6·5.
0·1549 „ 0·4220 CO_2 „ 0·0892 H_2O. C = 74·3; H = 6·4.
$C_{14}H_{14}OSi$ requires C = 74·2; H = 6·2 per cent.

It seemed clear from these observations that the supposed hydrol had been converted in a normal manner into the corresponding ketone (the termolecular form, p. 439), and that the melting point given by

Dilthey was incorrect; further experiments, however, led to the discovery of another hydrol, probably identical with the compound obtained by Dilthey.

β-Dibenzylsilicol, $Bz_2Si(OH)_2$.

On attempting to prepare a further quantity of ketone in the same manner as before, namely, by heating the α-hydrol (m. p. 101°) at 110° for several hours, an altogether different result was obtained; a solution of the oily residue in light petroleum deposited, not the ketone, but a crystalline substance, melting at 65—70°. This product was repeatedly recrystallised, the best results being obtained by dissolving it in a very little ether and adding a considerable quantity of light petroleum; it was then deposited, in the course of about half an hour, in beautiful, transparent prisms, which melted at 75°, softening at 70°. Repeated recrystallisation failed to render the melting point more precise, although to all appearance the preparation was quite pure. Unless the recrystallisation was carried out rapidly, and at a low temperature, some slight decomposition occurred, and the mother liquor deposited a small quantity of an oil. Analyses of samples dried in the air gave results which agreed with those required for the hydrol, $Bz_2Si(OH)_2$, although the percentage of carbon was always a trifle too high:

I. 0·1760 gave 0·4457 CO_2 and 0·1076 H_2O. C = 69·1; H = 6·8.
II. 0·1554 „ 0·3946 CO_2 „ 0·0934 H_2O. C = 69·2; H = 6·7.
III. 0·1711 „ 0·4334 CO_2 „ 0·1026 H_2O. C = 69·1; H = 6·7.
$C_{14}H_{16}O_2Si$ requires C = 68·7; H = 6·5 per cent.

Sample III was prepared by crystallising sample II three times from ether and light petroleum.

Molecular weight determinations made by the cryoscopic method gave the following results:

0·514 in 16·5 benzene gave Δt – 0·290°. Mol. wt. = 540.
0·703 „ 17·4 „ „ „ 0·360°. „ „ = 560.
0·287 „ 22·4 acetic acid „ „ 0·190°. „ „ = 260.
0·844 „ 17·8 „ „ „ „ 0·700°. „ „ = 263.
$C_{14}H_{16}O_2Si$ requires Mol. wt. = 244.

Most of the substance was recovered apparently unchanged when the benzene and acetic acid solutions were allowed to evaporate, but a trace of the oily decomposition product (see above) had doubtless been formed.

As this compound melting at 75° was thus found to be isomeric with the α-hydrol melting at 101°, it was natural to suppose that the two substances were merely different crystalline forms of one and the same substance. This view, however, had to be abandoned; samples of the two different preparations were crystallised under exactly the same conditions from a mixture of ether and light petroleum, but each retained its own distinctive properties. It was also found later that the two compounds could be deposited side by side from one and the same solution.

In one experiment, a fresh sample of dibenzylsilicon dichloride, boiling at 241—245° (100 mm.), prepared as before (which, although apparently pure, could not be crystallised), was decomposed with water and the product extracted with ether. When the solution was left to evaporate spontaneously, instead of becoming almost solid from the separation of pure α-hydrol, it deposited the β-hydrol in fine, large crystals, which, after recrystallisation from ether and light petroleum, melted at 75°, softening at about 70°. On the addition of light petroleum to the oily mother liquor, the whole became a thick paste of what seemed to be a mixture of the two forms of the hydrol. Attempts to separate these by recrystallisation were not very successful, as their solubilities were practically the same in all solvents, but at last a small quantity of the α-hydrol was isolated in a moderately pure condition.

Conversion of the β-Hydrol into Dibenzylsilicone.

The conversion of the β-dibenzylsilicol into the corresponding silicone seemed at first an extremely simple operation. A small quantity of the pure compound was gently heated in a test tube over a bunsen flame until the escape of water vapour ceased, and the resulting oil was dissolved in light petroleum; on cooling, the solution deposited crystals of pure dibenzylsilicone (m. p. 97—98°). On repeating the experiment with the same sample of β-hydrol under as nearly as possible the same conditions, instead of the silicone, the original β-hydrol was finally deposited from the light petroleum solution; several further similar experiments also gave this result, in spite of the fact that the water produced during the heating of the hydrol was clearly visible on the sides of the test tube. Many other attempts were made to transform the β-hydrol into the silicone; for example, the compound was heated at 150° for five minutes in an open dish, but, on crystallising the residue from light petroleum, practically the whole of the hydrol was ultimately recovered, although mixed with some oily product. Only in a few cases did we obtain any crystalline silicone.

Formation of the β-Hydrol from Dibenzylsilicone.

These perplexing results were explained to some extent by the discovery of the extraordinary fact that the oily product formed by the dehydration of the β-hydrol combines readily with water, the β-hydrol being regenerated. When the pure β-hydrol is kept in a vacuum over sulphuric acid at the ordinary temperature, it is converted in the course of about twenty-four hours into a very viscous, colourless oil; when this oil is exposed again to moist air, it is slowly reconverted into the β-hydrol, and if rubbed with a little water the change takes place in a few minutes.

Further Experiments on the Conversion of the Hydrols into the Silicone.

Quantitative experiments on the transformation of the β-hydrol into silicone at the ordinary temperature were not attempted, as the oily silicone formed at the surface prevents the decomposition of the crystals underneath; such experiments, however, carried out at 100° showed that after about seventy hours' heating the weight became practically constant, the loss being 6·6 instead of 7·4 per cent. as required by theory. Although the transformation of the hydrol into the silicone is a very simple change theoretically, and the last experiment seemed to show that it occurred almost quantitatively, some of our observations are not easily explained; thus the oil obtained by heating the β-hydrol at 100° did not give either crystalline silicone or β-hydrol when it was dissolved in ether and light petroleum or rubbed with water, differing in this respect from the oily silicone obtained in a vacuum at the ordinary temperature. Further, we have not been able to elucidate the nature of the oil which is produced in small quantities when the pure hydrol is recrystallised from various solvents, except that in some cases we have obtained from it the crystalline silicone by heating at 100°. It seems tolerably certain that, whereas the dehydration of the β-hydrol at the ordinary temperature leads simply to the formation of a unimolecular oily silicone which readily recombines with water, the effects of heating are more complex and lead to the formation of the termolecular crystalline silicone as well as that of other compounds.

The α-hydrol differs notably from the β-isomeride in stability; when kept over sulphuric acid in a vacuum, it does not change appreciably in appearance, although it becomes somewhat sticky in the course of a few days. A quantitative experiment on the decomposition of the α-hydrol (m. p. 101°) gave unsatisfactory results. The pure compound was heated at 110° in an open vessel; the weight decreased slowly and fairly regularly until after about twenty-five hours the theoretical loss (7·4 per cent.) for the formation of silicone had taken place; after about twenty-five hours' further heating, the loss amounted to about 11 per cent., but even then the weight of the oily product showed no sign of becoming constant. In no case have we been able to regenerate the α-hydrol from the product of its dehydration.

Action of Acetyl Chloride and Acetic Anhydride on the Hydrols.

Having failed to ascertain the precise conditions necessary for the conversion of the hydrols into the crystalline silicone by the action of heat alone, we studied their behaviour towards acetyl chloride and acetic anhydride.

Both compounds dissolved readily in acetyl chloride, but, on allowing their solutions to evaporate, they were finally both recovered unchanged; in the case of the β-hydrol, it is quite possible that the oily unimolecular silicone had really been formed, but that it absorbed water again on exposure to the air. When, however, the hydrols were separately heated in test tubes over a free flame until the ebullition caused by the escape of water ceased, and the residue then warmed with a little acetic anhydride, they were converted, apparently almost quantitatively, into crystalline dibenzylsilicone. These experiments with acetic anhydride were repeated several times with fairly constant results.

The molecular weight of the crystalline dibenzylsilicone, obtained in this way from the β-hydrol, was determined, and the results showed that the compound had the termolecular formula $(Bz_2SiO)_3$; the ebullioscopic method was used, with benzene as solvent:

0·585 in 14·0 benzene gave $\Delta t - 0·18°$. Mol. wt. = 620.
0·92 „ 14·0 „ „ „ 0·30°. „ = 587.
0·96 „ 13·0 „ „ „ 0·29°. „ = 674.
0·845 „ 14.3 „ „ „ 0·21°. „ = 737.

$(Bz_2SiO)_3$ requires Mol. wt. = 678.

A part of the expense incurred in this research has been met by a grant from the Government Grant Committee of the Royal Society, for which the authors express their gratitude.

UNIVERSITY COLLEGE,
NOTTINGHAM.

XLIV.—*Organic Derivatives of Silicon. Part VI. The Optically Active Sulphobenzylethylpropylsilicyl Oxides.*

By Frederic Stanley Kipping.

In Part II of these investigations (Trans., 1907, **91**, 209), it was stated that the *dl*-sulphonic acid obtained by heating benzylethylpropylsilicol with sulphuric acid had been resolved into its optically active components by fractionally crystallising its salt with *d*- or *l*-methylhydrindamine. Granting the accuracy of the experimental data there recorded, no further proof of the optical activity of the silicon compounds in question was required; to some, however, the author may have failed to carry conviction for various reasons. Firstly, because the *d*- and *l*-acids were only very feebly optically active; secondly, because the rotation was of the same sign as that of the base with which the acid had been combined; and, thirdly, because the salts of the active acids with *l*-menthylamine were practically identical in melting point and specific rotation.

In these circumstances, it seemed desirable to repeat the experiments on the resolution of the *dl*-acid with larger quantities of material, and to study in more detail the properties of the active compounds. The results of this work are described in the present communication, and they confirm in every respect the earlier observations. They have also shown that the salts formed by combining the *d*- and *l*-silicon acids with *d*-bornylamine or with cinchonidine resemble one another very closely, just as do their salts with *l*-menthylamine. This resemblance between compounds of the type *dAdB* and *lAdB* is so contrary to general experience, that before describing these salts it is advisable, perhaps, to summarise the results of those experiments which, having been repeated many times, establish the asymmetry of the acids concerned.

The *d*-methylhydrindamine salt of the pure *dl*-sulphonic acid is relatively easily separated by fractional crystallisation into two very different substances: the *dAdB*-salt is obtained in an optically pure state, melting at 205—207°; the optically impure *lAdB*-salt remains as an oil. Alkaline solutions obtained by boiling the *dAdB*-salt with excess of sodium carbonate until the organic base ceases to be evolved are always *dextrorotatory*, the highest observed specific rotation calculated for the sodium salt being +5·8°.

Alkaline solutions prepared from the optically impure *lAdB*-salt in a similar manner are *lævorotatory*; as methylhydrindamine is volatile and has a strongly alkaline reaction to litmus, its absence from a given solution is easily proved.

The sodium salt of the *d*-acid can be isolated from the dextrorotatory solutions; it crystallises from methyl alcohol in plates, and is optically active. With excess of *d*-methylhydrindamine hydrochloride in aqueous solution it gives a precipitate which is practically identical with the original *dAdB*-salt melting at 205° (compare p. 465), but with *l*-methylhydrindamine hydrochloride, under exactly similar conditions, it gives a totally different precipitate, namely, the *dAlB*-salt, a gelatinous substance melting at 150—152°.

The sodium salt obtained from the oily, optically impure *lAdB*-salt gives with *l*-methylhydrindamine hydrochloride in aqueous solution a precipitate from which a considerable proportion of the *lAlB*-compound (m. p. 205°) can be isolated.

The *dl*-sulphonic acid may be resolved with *l*-methylhydrindamine; the optically pure *lAlB*- and impure *dAlB*-salts thus obtained correspond in properties with the *dAdB*- and *lAdB*-salts respectively, the observed rotations being, of course, of the opposite sign.

A mixture of the *dAdB*- and *lAlB*-salts, and also a mixture of the *dAlB*- and *lAdB*-salts, has the properties of the substance prepared directly from the *dl*-acid and *dl*-base (compare *loc. cit.*, pp. 237—238). The acids represented by *dA* and *lA* respectively are thus proved to be optically active and enantiomorphously related.

In spite of this relationship and the great difference in outward properties of their salts with one of the active methylhydrindamines, solutions of the sodium salts of the two active acids yield, with a given optically active base, compounds which in many cases are barely distinguishable from one another or from the corresponding derivative of the *dl*-acid.

This resemblance is not restricted to appearance and crystalline habit, but extends to melting or decomposing point and even to specific rotation, as will be seen from the following summary of some of the results of the examination of such compounds.

Salts of d- *and* l-*Sulphobenzylethylpropylsilicyl Oxides*,

$$SO_3H\cdot CH_2\cdot C_6H_4\cdot SiEtPr\cdot O\cdot SiEtPr\cdot CH_2\cdot C_6H_4\cdot SO_3H.$$

d-*Methylhydrindamine Salts*:

d-Acid.	*l*-Acid.
M. p. 205—207°	M. p. 150—152°
$[\alpha]_D$ +15·6° in methyl alcohol	$[\alpha]_D$ +15·6° in methyl alcohol
$[\alpha]_D$ +14·4° in chloroform	

l-*Methylhydrindamine Salts :*

d-Acid.	*l*-Acid.
M. p. 150—152°	M. p. 205—207°
$[\alpha]_D$ −15·6° in methyl alcohol	$[\alpha]_D$ −15·3° in methyl alcohol
	$[\alpha]_D$ −14·8° in chloroform

l-*Menthylamine Salts :**

d-Acid.	*dl*-Acid.	*l*-Acid.
M. p. 228—229°	M. p. 225—226°	M. p. 226—227°
M. p. 235—236°	M. p. 233—235°	M. p. 236—237°
$[\alpha]_D$ −15·6°†	$[\alpha]_D$ −15·5°	$[\alpha]_D$ −15·5°

* These salts are dimorphous.

† This and all the following values for specific rotation were determined in methyl-alcoholic solution.

d-*Bornylamine Salts :*

d-Acid.	*dl*-Acid.	*l*-Acid.
M. p. 210—211°	M. p. 207—208°	M. p. 212—213°
$[\alpha]_D$ +9·2°	$[\alpha]_D$ +9·8°	$[\alpha]_D$ +9·6°

Cinchonidine Salts :

d-Acid.	*dl*-Acid.	*l*-Acid.
M. p. 154—156°	M. p. 148—150°	M. p. 149—150°
$[\alpha]_D$ −71·5°	$[\alpha]_D$ −73·1°	$[\alpha]_D$ −71·6°

Cinchonidine Hydrogen Salts :

d-Acid.	*dl*-Acid.	*l*-Acid.
M. p. 222—224°	M. p. about 220°	M. p. 225—227°

The dissimilarity of the methylhydrindamine salts of the type *dAdB* and *dAlB* is even more striking than appears from the tabulated data ; the pure *dAdB*- and *lAlB*-compounds crystallise readily in radially grouped clusters of characteristic appearance and of high density ; the *dAlB*- and *lAdB*-salts, on the other hand, can hardly be said to crystallise, as they separate from most solvents in the form of a bulky jelly.

The *l*-menthylamine salts of the *d*- and *l*-acids can hardly be distinguished from one another ; this is also true of the *d*-bornylamine salts, whereas the normal cinchonidine and the cinchonidine hydrogen salts show small differences in melting point, but are otherwise very much alike.

These observations are instructive and of general interest, because they indicate that it might be possible actually to resolve a *dl*-compound by the usual method, and yet to conclude from an examination of the outward properties and specific rotations of the several fractions so obtained that resolution had not occurred; if, for example, the *l*-menthylamine salt of *dl*-sulphobenzylethylpropylsilicyl oxide could in fact be separated into its *dAlB*- and *lAlB*-components, the greatest difference between extreme fractions which would be brought to light by the ordinary methods of examination would be about 1° in melting point.

It is obvious, of course, that the very close resemblance observed between some of the salts referred to above would be merely a necessary consequence if the active acids underwent partial or complete racemisation subsequent to their separation from the methylhydrindamine used for their isolation. For this reason, the possibility of racemisation was considered at an early stage of the work. The fact that the ammonium salt of either of the active acids afforded such different compounds with *d*- and *l*-methylhydrindamine hydrochlorides (*loc. cit.*, p. 236) showed conclusively that the acids had not racemised to any great extent, and similar observations with the sodium salts (see above) confirmed the conclusion that the active compounds were relatively stable.

Nevertheless, in the course of these experiments, it was found that during the conversion of the *dAdB*- or *lAlB*-methylhydrindamine derivative into the sodium salt by heating with excess of sodium carbonate during some hours, a change of some kind took place, because, on regenerating the methylhydrindamine salt by precipitation, the melting point of the crude substance was sometimes considerably lower than that of the original pure resolution product. Whether this is really due to racemisation or to decomposition has not yet been ascertained, as the principal object of these experiments was to study the active acids; with this end in view, the methylhydrindamine salts were very cautiously treated with sodium carbonate, the period of heating being limited as far as possible; under these conditions, little, if any, change in the acids takes place, and it was from such preparations of the active sodium salts that the various compounds now to be described, including the *dAlB*- and *lAdB*-methylhydrindamine derivatives, were obtained.

During the investigation of these optically active acids, two points connected with their constitution have also received attention.

Further evidence has been published (Marsden and Kipping, this vol., p. 198) supporting the author's previous conclusion that the acids are derivatives of benzylethylpropylsilicyl oxide and not of the corresponding silicol, and it is shown in this paper that the sulphonic groups in the acids occupy the para-positions in the two benzene nuclei. This last point is important, as it proves that the optical activity of the compounds is not due to the presence of an asymmetric carbon group, which, conceivably, might have been formed by the displacement of hydrogen from one of the $\cdot CH_2\cdot$ groups contained in the oxide.

EXPERIMENTAL.

Further experience in the preparation of sulphobenzylethylpropylsilicyl oxide has brought out certain improvements in the methods, which may be briefly mentioned. In decomposing benzylethylpropylsilicyl chloride (Trans., 1907, **91**, 726), the yield of the corresponding silicol *seems* to be very much increased, and that of the oxide diminished, when the chloride is dropped fairly quickly from a tap-funnel into an ice-cold saturated solution of sodium carbonate instead of into water. The alkaline solution is vigorously shaken during and after the addition of the chloride until decomposition is complete, and the product is then immediately extracted with ether. The separation of the silicol from the oxide by fractional distillation under reduced pressure is easily accomplished, and, when the whole series of operations is carried out as quickly as possible, the yield of the former may amount to about 85 per cent. of the theoretical. Whether this is due to the use of sodium carbonate, or to the silicol not having been given time to pass into the oxide, has not been ascertained; according to previous observations (*loc. cit.*), the silicol may change spontaneously into the oxide and water when it is kept at the ordinary temperature, and, therefore, it is advisable to sulphonate it without delay. It is advantageous to obtain as much silicol as possible at the expense of the oxide, because, although the *dl*-sulphonic acid is actually derived from the oxide, it is far more easily isolated from the product of the sulphonation of the silicol (compare Marsden and Kipping, *loc. cit.*); this curious fact has not yet been accounted for experimentally, but may be attributed to a difference in the nature of the by-products in the two cases.

The process of sulphonation has been modified to some extent; the silicol and sulphuric acid (2 vols.) are vigorously shaken together in a flask, and the emulsion, the temperature of which is raised to 40° or 50° by the spontaneous heat development, is rapidly warmed in a metal-bath to 80°, when it is again well shaken. Sulphonation is complete within about one minute, and the contents of the flask are then immediately cooled and poured into water. The *dl*-acid may then be isolated in the form of its ammonium salt (*loc. cit.*, p. 225), or the solution of the latter may be directly precipitated with *l*-menthylamine hydrochloride. The reduction of the temperature from 100° to 80° during sulphonation seems to have a marked effect on the nature of the product; the yield of pure ammonium salt seems to be greater, and the *l*-menthylamine salt obtained by precipitating the crude product, although not a homogeneous substance, crystallises readily from moist ethyl acetate, and furnishes pure *l*-menthylamine sulphobenzylethylpropylsilicyl oxide after several recrystallisations.

The by-products obtained in the sulphonation of the silicol and the oxide still await investigation.

Resolution of the dl-*Acid.*

The whole of the *dl*-acid used in these resolution experiments was prepared from the pure *l*-menthylamine salt, most of which had been isolated from the product of the sulphonation of the oxide (Marsden and Kipping, *loc. cit.*); some of the *l*-menthylamine salt, however, was prepared from the product of the sulphonation of the silicol. The active methylhydrindamines were obtained by resolving the *dl*-base with *d*-bromocamphorsulphonic acid (Tattersall and Kipping, Trans., 1903, **83**, 918) or with *d*-tartaric acid, and in the latter case the active bases were obtained optically pure by converting them into their *d*-bromocamphorsulphonates.

A concentrated neutral solution of the sodium salt of the *dl*-acid is treated with excess of the hydrochloride of the *d*-base, and the oily precipitate is left to solidify; it is then separated by decantation, washed with water, and crystallised from aqueous methyl alcohol at the ordinary temperature. The first deposit is often like putty, consisting of a fine, heavy powder impregnated with oil; as fractional crystallisation proceeds, the crude *lAdB*-salt in the filtrates becomes more oily, the more sparingly soluble *dAdB*-salt more coarsely crystalline, and after a series of operations the salt of the *d*-acid is obtained in a pure state.

The resolution of the *dl*-acid with *l*-methylhydrindamine affords, of course, the pure *lAlB*-salt and oily fractions of crude *dAlB*-salt.

The optically impure *lAdB*- and *dAlB*-derivatives which are obtained in these resolutions are separately decomposed with sodium carbonate as described below, and the resulting solutions, which are lævorotatory and dextrorotatory respectively, are treated with *l*- and with *d*-methylhydrindamine hydrochloride respectively in order to obtain further quantities of the *lAlB*- and *dAdB*-salts. In this way, employing the *d*- and *l*-bases alternately, it is possible to resolve a very large proportion of the *dl*-acid into its pure *dAdB*- and *lAlB*-derivatives. During these prolonged operations, however, owing to atmospheric oxidation or some decomposition, the solutions often become brown, especially when they have been heated for some time, and the *d*- or *l*-methylhydrindamine salts, prepared from the oily *dAlB*- and *lAdB*-compounds respectively, cannot be crystallised.

Accordingly, the precipitate is roughly dried and dissolved in boiling acetone, from which the crude *dAdB*- or *lAlB*-salt is then usually deposited as a colourless powder, on evaporating over sulphuric acid; this preparation is afterwards fractionally crystallised from slightly moist acetone or from aqueous methyl alcohol as before. The crude sodium salts obtained by decomposing the *lAdB*- and *dAlB*-derivatives may also be purified by crystallisation from aqueous methyl alcohol before precipitating with the required methylhydrindamine hydrochloride.

d-*Methylhydrindamine* d-*Sulphobenzylethylpropylsilicyl Oxide*, $SO_3H\cdot C_6H_4\cdot CH_2\cdot SiEtPr\cdot O\cdot SiEtPr\cdot CH_2\cdot C_6H_4\cdot SO_3H,2C_{10}H_{13}N$.

This compound separates from warm aqueous methyl alcohol in small, transparent prisms, but, when crystallisation takes place slowly at the ordinary temperature, the salt is deposited in highly characteristic, round masses of radially grouped prisms; it is anhydrous and melts at 205—207°, decomposing to a slight extent. It is very readily soluble in the common alcohols, and in moist acetone, and also dissolves freely in chloroform, but it is almost, if not quite, insoluble in anhydrous acetone, ethyl acetate, or cold water.

Its specific rotation was determined in methyl-alcoholic solution in a 2-dcm. tube:

1·062 grams, made up to 25 c.c., gave $\alpha + 1{\cdot}33°$; whence $[\alpha]_D + 15{\cdot}6°$.

This value agrees with those ($+15{\cdot}6°$, $16{\cdot}0°$) previously obtained (*loc. cit.*, p. 235) with much more dilute solutions; the substitution of water for some of the methyl alcohol did not appreciably alter the specific rotation.

Its specific rotation in chloroform solution was also determined:

0·904 gram, made up to 25 c.c. in a 2-dcm. tube, gave $\alpha + 1{\cdot}04°$; whence $[\alpha]_D + 14{\cdot}4°$.

l-*Methylhydrindamine* l-*Sulphobenzylethylpropylsilicyl Oxide*.

The ordinary properties of this salt are identical of course with those of its optical antipodes. Its specific rotation was determined (*a*) in methyl-alcoholic and (*b*) in chloroform solutions:

(*a*) 0·925 gram, made up to 25 c.c. in a 2-dcm. tube, gave $\alpha - 1{\cdot}14°$; whence $[\alpha]_D - 15{\cdot}3°$.

(*b*) 0·888 gram, made up to 25 c.c. in a 2-dcm. tube, gave $\alpha - 1{\cdot}05°$; whence $[\alpha]_D - 14{\cdot}8°$.

Sodium Salts of the Active Acids.

The preparation of the sodium salts from the pure methylhydrindamine derivatives of the optically active acids, theoretically the simplest operation, is, in fact, rather troublesome. The organic base cannot be expelled by boiling with sodium hydroxide, as the acid is thereby decomposed (p. 472); even sodium carbonate, if used in excess, brings about some decomposition or racemisation, and has also the disadvantage that it gives the less readily volatile carbonate instead of free methylhydrindamine.

In the earlier experiments, the methylhydrindamine salts were separately treated with excess of sodium carbonate, and the carbonate of the organic base volatilised in steam; as it was essential that every trace of the methylhydrindamine should be expelled before observing the rotation of the acid, and as the alkaline solutions frothed very much, the distillation in steam was necessarily prolonged; as, further, the solutions were afterwards concentrated by evaporating on the water-bath, the active acids were exposed for a long time to the combined action of the organic and inorganic bases. Under these conditions, solutions were obtained which gave the rough values $[\alpha]_D + 3{\cdot}3^\circ$ and $+ 4{\cdot}2^\circ$ for the sodium salt of the *d*-acid, and $[\alpha]_D - 4{\cdot}5^\circ$ for that of the *l*-acid.

Although such solutions were invariably tested before the optical examination and found to be free from methylhydrindamine, it seemed desirable to isolate the sodium salts of the active acids in order to afford indisputable evidence that the observed rotations were due to the silicon compounds alone.

For this purpose, and with the object of avoiding prolonged heating, the pure *dAdB*- and *lAlB*-salts were separately treated with an aqueous solution containing a slight excess of sodium carbonate, and the methylhydrindamine carbonate extracted by repeatedly shaking with ether; the aqueous solutions were then evaporated almost to dryness, neutralised with acetic acid, and mixed with excess of methyl alcohol. The precipitated sodium salts were separated by filtration, washed well with methyl alcohol, dissolved in a very little water, reprecipitated with methyl alcohol, and dried in the air.

The *sodium* salts thus obtained crystallise in lustrous plates or prisms, and are extremely soluble in cold water, but only sparingly so in cold methyl alcohol; when dried in the air, they contain water of crystallisation, as shown by the following analysis of the salt of the *d*-acid:

1·457 lost 0·084 at 100°. $H_2O = 5{\cdot}76$.

$C_{24}H_{36}O_7S_2Na_2Si_2,2H_2O$ requires $H_2O = 5{\cdot}63$ per cent.

The specific rotations of the anhydrous salts were determined in aqueous solution:

Salt of *d*-acid: 1·37 grams, made up to 20 c.c. in a 2-dcm. tube, gave $\alpha + 0·72°$; whence $[\alpha]_D + 5·2°$.

Salts of *l*-acid: 0·5 gram, made up to 25 c.c. in a 2-dcm. tube, gave $\alpha - 0·17°$; whence $[\alpha]_D - 4·2°$.

Although these values did not agree very well (the experimental error in the latter case may have been considerable), the determinations were not repeated, as there was no object in isolating the sodium salts, except to prove that they were optically active.

Higher and more concordant values for the specific rotations of these salts were obtained in the following manner. A weighed quantity (2—3 grams) of the pure *dAdB*- or *lAlB*-salt is dissolved in ethyl alcohol, treated with a slight (about 5 per cent.) excess of crystallised sodium carbonate, and the methylhydrindamine volatilised in a rapid current of steam, the distillation flask being directly heated over a free flame; the troublesome frothing of the solution is thus almost entirely prevented, and the whole of the organic base may be expelled in about fifteen minutes; the boiling solution is then transferred to an evaporating basin, concentrated to about 10 c.c., neutralised with acetic acid, and cooled; after filtering from traces of a flocculent substance, the filtrate and washings are made up to 20 c.c. In a 2-dcm. tube:

2·85 grams *dAdB* (= 2·01 grams of sodium salt) gave $\alpha + 1·18°$; whence $[\alpha]_D + 5·8°$.

2·90 grams *lAlB* (= 2·05 grams of sodium salt) gave $\alpha - 1·20$; whence $[\alpha]_D - 5·9°$.

These specific rotations are calculated for the sodium salts, and are the highest and, doubtless, the most trustworthy values which have been obtained.

Partial Racemisation or Decomposition of the Active Acids.

Under the conditions just described, the alkaline solutions of the sodium salts of the active acids are only heated during about forty-five minutes at the very most, and little, if any, change occurs in the acids themselves; this is proved by the fact that, when the *dAdB*- or *lAlB*-salt is prepared again from the solution of the sodium salt by adding the required hydrochloride of *d*- or *l*-methylhydrindamine, the product, after having been merely washed with water and dried, melts at practically the same temperature as the original compound. When, on the other hand, in decomposing the methylhydrindamine salt, the active acid has been heated in alkaline solution during a much longer period, the crude, regenerated methylhydrindamine salt may begin to sinter at about 185° and melt at about 190°, an indication that partial racemisation has occurred.

This evidence is corroborated by the values obtained, in the earlier determinations, for the specific rotations of the sodium salts prepared without the above precautions having been taken. When such solutions of the sodium salts are fractionally precipitated with methyl alcohol, the sparingly soluble fractions seem to consist of the optically pure salt, the *dl*-compound remaining for the most part in the mother liquors.

Although, therefore, there is some evidence that racemisation occurs when the acid is heated for some time in presence of methylhydrindamine and sodium carbonate, the matter has not been very carefully studied, and the observed changes may possibly be due to decomposition; the principal object in view was to obtain the sodium salts of the optically pure active acids, and this seems to have been attained in the manner described above.

Metallic Salts of the Active Acids.

The ***barium*** salts of the active acids, like that of the *dl*-compound, are well-crystallised substances, practically insoluble in water, but readily soluble in hot aqueous alcohol.

The ***calcium*** salt is precipitated as an oil on adding calcium chloride to an aqueous solution of the sodium salt; it is soluble in hot water and in cold aqueous methyl alcohol.

The ***lead*** salt is readily soluble in boiling water, and separates on cooling in highly lustrous plates.

l-*Methylhydrindamine* d-*Sulphobenzylethylpropylsilicyl Oxide.*

On adding excess of *l*-methylhydrindamine to the sodium salt of the *d*-acid in aqueous solution, there results an oily precipitate which shows no tendency to crystallise, but which gradually changes to a rather pasty or gelatinous solid when it is stirred. This salt is practically insoluble in water in presence of sodium chloride and *l*-methylhydrindamine hydrochloride, but, when it has been washed by decantation, it dissolves to a considerable extent; the cold aqueous solution first becomes turbid and then clear again when it is warmed, and it is also changed to a milky fluid on the addition of a little methyl alcohol or sodium chloride. The salt is very readily soluble in methyl alcohol, from which it is precipitated as an oil on adding water, but from dilute solutions in highly aqueous methyl alcohol it separates in flocculent masses which seem to consist of threads of gelatinous spheres. It dissolves freely in hot acetone in presence of traces of water, and, on cooling, the solution sets to a stiff jelly, which changes to a friable solid when kept over sulphuric acid until all the solvent has evaporated; it shows a similar behaviour towards moist ethyl acetate, and is also precipitated from this solvent as a jelly on the addition of light petroleum. Solutions in highly aqueous acetone, when evaporated at the ordinary temperature, set to an opalescent mass, in which after some time white patches appear and gradually spread, just as if a mould were growing in a nutritious medium.

The friable solid obtained with the aid of acetone sinters a little at about 148°, and is completely melted at about 152°, but, as no satisfactory method of purifying the salt was discovered, it is possible that its melting point may be a little higher.

For the determination of its specific rotation, the solid, from acetone, was dried at 100° and examined in methyl-alcoholic solution:

0·754 gram, made up to 20 c.c. in a 2-dcm. tube, gave $\alpha - 1{\cdot}18°$; whence $[\alpha]_D - 15{\cdot}6°$.

Attention has already been drawn to the great contrast between this salt and the *lAlB*-derivative in outward properties, and yet the two compounds have the same specific rotation in methyl-alcoholic solution; this is also true in the case of other pairs of salts of the type *dAlB* and *lAlB*, the rotation being apparently unaffected by the molecule of the acid.

d-*Methylhydrindamine* l-*Sulphobenzylethylpropylsilicyl Oxide.*

This salt, prepared by precipitating a solution of the sodium salt of the *l*-acid with *d*-methylhydrindamine hydrochloride, is, of course, identical with its optical antipodes in ordinary properties; its specific rotation in methyl-alcoholic solution ($[\alpha]_D + 15{\cdot}6°$) has been given before (*loc. cit.*, p. 235), and, although the specimen there used was probably not quite free from *dAdB*-salt, it seemed unnecessary to repeat the determination, as the optical impurity has practically the same rotation.

When the *lAdB*- and *dAlB*-methylhydrindamine salts are mixed together in aqueous alcohol and the solution is allowed to crystallise at the ordinary temperature, it deposits a fine, white powder, totally different in outward properties from the gelatinous *lAdB*- and *dAlB*-salts; this powder, when dried in the air, melts indefinitely at temperatures varying from about 175° to 185°, that is to say, its behaviour is the same as that of the salt prepared by mixing or crystallising together the *dAdB*- and *lAlB*-methylhydrindamine salts. The behaviour of a mixture of the *dAdB*- and *lAlB*-compounds has also been examined again, and the results fully confirmed previous observations (*loc. cit.*, p. 237).

l-*Menthylamine* d-*Sulphobenzylethylpropylsilicyl Oxide.*

This compound is obtained as a crystalline precipitate on adding *l*-menthylamine hydrochloride to the sodium salt of the *d*-acid in aqueous solution; it crystallises well from aqueous methyl alcohol or from moist ethyl acetate, and melts at 228—229° (see below):

0·6493 of air-dried salt lost 0·0490 at 100°. $H_2O = 7·5$.

$C_{44}H_{80}O_7N_2S_2Si_2,4H_2O$ requires $H_2O = 7·5$ per cent.

The specific rotation of the anhydrous salt was determined in methyl-alcoholic solution:

0·6 gram, made up to 20 c.c. in a 2-dcm. tube, gave $\alpha - 0·93°$; whence $[\alpha]_D - 15·6°$.

l-*Menthylamine* l-*Sulphobenzylethylpropylsilicyl Oxide.*

This salt is prepared from a solution of the sodium derivative of the *l*-acid in a similar manner; it crystallises well from aqueous methyl alcohol or moist ethyl acetate, and melts at 226—227° (see below):

0·6807 of air-dried salt lost 0·0525 at 100°. $H_2O = 7·7$.

The specific rotation of the anhydrous salt was determined in methyl-alcoholic solution:

0·628 gram, made up to 20 c.c. in a 2-dcm. tube, gave $\alpha - 0·97°$; whence $[\alpha]_D - 15·5°$.

The *l*-menthylamine salts of the *l*- and *d*-acids resemble one another very closely, and are also almost indistinguishable from the salt of the *dl*-acid, which crystallises with 4 molecules of water and has a specific rotation $[\alpha]_D - 15·5°$ in methyl-alcoholic solution (*loc. cit.*, p. 229). The three compounds were separately crystallised from aqueous methyl alcohol and from moist ethyl acetate under similar conditions and compared directly, but the only slight difference which could be observed was that the salt of the *l*-acid seemed to form rather smaller crystals than the other two. The melting points of the three salts were also compared directly; employing samples crystallised from aqueous methyl alcohol and dried at 100°, and heating in the ordinary way, that of the *dl*-acid* always melted first at 225—226°, followed by that of the *l*-acid at 226—227°, that of the *d*-acid melting last at 228—229°. These values are rather relative than absolute, as, probably owing to slight decomposition, the melting points are not very sharp. When samples of the salts obtained from moist ethyl acetate and dried in the air are heated in a similar manner, they show the behaviour just recorded; when, however, such samples are first suddenly heated at about 160°, they immediately melt more or less in their water of crystallisation, and then solidify again; if the temperature is then raised gradually, the salt of the *dl*-acid melts at 233—235°, followed by that of the *d*-acid at 235—236°, that of the *l*-acid melting last at 236—237°. This alteration of the melting point according to the rate of heating is no doubt due to dimorphism of the anhydrous salts; it is not always observed, and sometimes melting extends over several degrees, as if the one crystalline form were changing into the other, so that the sequence given above for the modifications of higher melting point is not invariable. These observations, however, seem to show conclusively that there is a difference, although a small one, between the salts of the *d*- and *l*-acids which is not due to the presence of optical impurity, as one crystalline form of the salt of the *d*-acid melts higher, the other lower, than that of the corresponding form of the salt of the *l*-acid. That the raising of the melting points when the salts are suddenly heated is not merely due to a difference in the extent of their decomposition is easily shown; if one of two tubes containing, say, the salt of the *dl*-acid is plunged for a moment into a bath at 160°, and then both are slowly and simultaneously heated from the ordinary temperature, the sample, which has not been previously heated, melts at 225—226°, the other at 233—235°.

---

* The salt of the *dl*-acid was prepared by precipitation from a carefully purified specimen of the ammonium salt, and was only recrystallised once, so that it doubtless contained equal quantities of the *dAlB*- and *lAlB*-compounds.

This variable and not very definite melting point of the salt of the *dl*-acid has been repeatedly observed, and was thought to be due to decomposition or to the fact that the salt was a mixture of components, the relative proportions of which might be altered to some extent by repeated crystallisation (Marsden and Kipping, *loc. cit.*); for this reason, the average value of the melting point (about 230°) was previously given. The melting point (about 230°) previously assigned to the *l*-menthylamine salt of the optically impure *l*-acid (*loc. cit.*, p. 235) is probably that of a mixture of the two *lAlB*-salts, melting at 226—227° and 236—237° respectively.

Further Attempts to Resolve the l-*Menthylamine Salt.*

It is conceivable that the *lAlB*- and *dAlB*-menthylamine salts might differ sufficiently in solubility to allow of their separation, and yet, owing to the similarity of the different fractions in outward and in optical properties, the fact that the *dl*-acid had been resolved might easily remain undiscovered. In the hope of being able to substitute *l*-menthylamine for the far less accessible active methylhydrindamines, some further experiments were made with this base; a sample of the salt of the *dl*-acid was crystallised several times from warm moist ethyl acetate, and then two or three times from hot anhydrous ethyl acetate containing a little methyl alcohol, until only a very small proportion of the original sample remained. This was converted into sodium salt, and the solution precipitated with *d*-methylhydrindamine hydrochloride; the crude air-dried product melted from 175—180°, and therefore consisted of a mixture of the *dAdB*- and *lAdB*-salts.

d-*Bornylamine* d-*Sulphobenzylethylpropylsilicyl Oxide.*

This salt is precipitated from a solution of the sodium salt of the *d*-acid as an oil, which soon solidifies and crystallises well from aqueous methyl alcohol; the air-dried compound is anhydrous, and melts at 210—211°; its specific rotation was determined in methyl-alcoholic solution:

0·705 gram, made up to 20 c.c. in a 2-dcm. tube, gave $\alpha + 0{\cdot}65°$; whence $[\alpha]_D + 9{\cdot}2°$.

d-*Bornylamine* l-*Sulphobenzylethylpropylsilicyl Oxide.*

This substance was prepared in a similar manner from the sodium salt of the *l*-acid; the air-dried crystals are anhydrous, and melt at 212—213°. The specific rotation was determined in methyl-alcoholic solution:

0·614 gram, made up to 20 c.c. in a 2-dcm. tube, gave $\alpha + 0{\cdot}59°$; whence $[\alpha]_D + 9{\cdot}6°$.

The *d*-bornylamine salts of the *d*-, *l*-, and *dl*-acids are very similar, and even when compared directly are almost indistinguishable; they all separate from aqueous methyl alcohol in lustrous prisms, but, when deposited under similar conditions, the salt of the *l*-acid seems always to give the smallest and least well-defined crystals. When heated side by side, the salt of the *dl*-acid melts first at 207—208°, then that of the *d*-acid at 210—211°, and finally that of the *l*-acid at 212—213°; the salts decompose a little, and their melting points seem to depend to some extent on the rate of heating, but recrystallisation failed to raise the melting point of the salt of the *l*-acid as high as that of the salt of the *d*-acid. The salt of the *dl*-acid used in these comparisons was prepared from pure ammonium *dl*-sulphobenzylethylpropylsilicyl oxide, and only crystallised once; the slightly higher melting point (208—210°) previously given for this compound may be the result of a difference in the rate of heating.

Cinchonidine Salts of the d- *and* l-*Acids.*

These compounds were prepared by precipitating solutions of the sodium salts of the active acids with cinchonidine hydrochloride, $C_{19}H_{22}ON_2,HCl,2H_2O$ (Merck); the oily precipitates were washed well with water, dried, and dissolved in anhydrous acetone containing a trace of methyl alcohol; the compounds separated as crystalline powders, consisting of small prisms, when these solutions were evaporated over sulphuric acid.

The specific rotations were determined in methyl-alcoholic solution with samples dried at 100°.

Salt of *d*-acid: 0·503 gram, made up to 20 c.c. in a 2-dcm. tube, gave $\alpha - 3{\cdot}60^\circ$; whence $[\alpha]_D - 71{\cdot}5^\circ$.

Salt of *l*-acid: 0·528 gram, made up to 20 c.c. in a 2-dcm. tube, gave $\alpha - 3{\cdot}78^\circ$; whence $[\alpha]_D - 71{\cdot}6^\circ$.

These values are practically the same as that ($[\alpha]_D - 73{\cdot}1^\circ$) obtained for the salt of the *dl*-acid in more dilute solutions.

The melting points of the salts were compared directly; that of the *l*-acid melted at 149—150°, that of the *d*-acid at 154—156°, whereas that of the *dl*-acid melts at 148—150° (*loc. cit.*, p. 232). The derivative of the *l*-acid was recrystallised from ethyl acetate containing methyl alcohol, but its melting point underwent no change, so that the cinchonidine salts of the active acids show a more considerable difference than either the *l*-menthylamine or the *d*-bornylamine derivatives; their melting points, however, are not very easily determined, as the melting substances give an opaque froth, apparently owing to the inclusion of air. The behaviour of the salts towards solvents is similar to that of the derivative of the *dl*-acid, and it may be noted that they are all practically insoluble in ethyl acetate in complete absence of moisture.

Cinchonidine Hydrogen Salts of the d- *and* l-*Acids.*

The normal salts of the active acids were separately converted into the hydrogen salts as described in the case of the derivative of the *dl*-acid (p. 233), and the washed precipitates were dried. The brittle, resinous masses so obtained were then dissolved in anhydrous acetone containing methyl alcohol, and the solutions evaporated over sulphuric acid. The salts were then deposited as colourless, microcrystalline powders. Their melting, or decomposing, points were compared directly, and, although they varied very considerably with the rate of heating, the salt of the *d*-acid always decomposed about 3° lower than that of the *l*-acid, and its melting point did not alter on recrystallising.

When heated in the ordinary way, the salt of the *d*-acid darkened at about 222°, and decomposed completely at about 224°; that of the *l*-acid darkened at about 225°, and decomposed completely at about 227°. When heated much more rapidly, the respective temperatures were about 3° higher in all cases. A coarse mixture of the two salts decomposed just before the derivative of the *d*-acid; the decomposition point of the salt of the *dl*-acid was previously given as 220° (*loc. cit.*).

Decomposition of dl-*Sulphobenzylethylpropylsilicyl Oxide.*

When, in isolating the *dl*-acid from the sulphonation of the oxide or of the silicol, the crude product is evaporated with excess of ammonia (*loc. cit.*, p. 225), the solution remains clear, and no sign of decomposition has ever been observed; even when solutions of the sodium salt of the acid are boiled with sodium carbonate during some time, only traces of a flocculent precipitate are formed. When, however, the acid is heated at 100° with excess of concentrated sodium hydroxide solution, it is slowly but completely decomposed, and the solution becomes turbid, owing to the separation of a viscous, insoluble silicon compound, which has not yet been examined. The alkaline solution, separated from the silicon compound by filtration, neutralised with acetic acid, and concentrated if necessary, gives with *l*-menthylamine hydrochloride an oily precipitate which soon solidifies, and which crystallises well from aqueous methyl alcohol in long, slender needles.

The air-dried salt (0·4285 gram lost 0·0428 gram at 100°) contained 10·0 per cent. of water of crystallisation, and the equivalent of the anhydrous compound, determined by titration, agreed with that required for the menthylamine salt of toluenesulphonic acid.

As it seemed highly probable that the soluble decomposition product of sulphobenzylethylpropylsilicyl oxide would be *p*-toluenesulphonic acid, some of the hydrocarbon was sulphonated with sulphuric acid and the resulting sulphonic acids converted into their *l*-menthylamine salts, but the fractional crystallisation of this preparation from aqueous methyl alcohol failed to separate the *o*- and *p*-isomerides. A sample of *p*-toluenesulphonic acid, obtained from Kahlbaum, was converted into its *l*-menthylamine salt, and the preparation dried in the air:

0·3181 lost 0·0321 at 100°. $H_2O = 10{\cdot}1$.

$C_{17}H_{29}O_3NS,2H_2O$ requires $H_2O = 9{\cdot}9$ per cent.

This specimen of *l*-menthylamine *p*-toluenesulphonate was indistinguishable in outward properties from that obtained from the product of the decomposition of sulphobenzylethylpropylsilicyl oxide; when heated side by side, the two preparations melted simultaneously at 201—202° (the former sintering a little at about 199°); a mixture of the two also melted at this temperature, and gave a homogeneous deposit when crystallised from aqueous methyl alcohol.

Further Experiments on the Resolution of dl-*Sulphobenzylethylpropylsilicyl Oxide.*

In the course of some of the earlier experiments on the resolution of the *dl*-acid, a solution of its sodium salt was precipitated with the hydrochloride of *l*-*iso*menthylamine (Tutin and Kipping, Trans., 1904, **85**, 65), and the product, which solidified in the course of a few days, was submitted to fractional crystallisation. From its solution in aqueous methyl alcohol or acetone, it was deposited as an oil, even at 0°, but it ultimately solidified again when nearly all the organic solvent had evaporated. A solution of the roughly-dried salt in anhydrous acetone, however, deposited a fine powder when evaporated over sulphuric acid, and the original preparation was in this way separated into four fractions. The first and last of these had practically the same melting point (160—162°) and the same specific rotation in 90 per cent. alcoholic solution:

I. 0·5466 gram, made up to 25 c.c. in a 2-dcm. tube, gave $\alpha + 0{\cdot}23^\circ$; whence $[\alpha]_D + 5{\cdot}3^\circ$.

IV. 0·4915 gram, made up to 25 c.c. in a 2-dcm. tube, gave $\alpha + 0{\cdot}23^\circ$; whence $[\alpha]_D + 5{\cdot}8^\circ$.

These results seemed to show that the *dl*-acid had not been resolved, and this conclusion was subsequently confirmed by examining the salts obtained by combining the acid from the first fraction with *d*- and with *l*-methylhydrindamine.

l-*iso*Menthylamine *dl*-sulphobenzylethylpropylsilicyl oxide does not crystallise well; it is practically insoluble in acetone in absence of moisture.

It may be mentioned, in conclusion, that the active hydrindamines cannot be successfully used in place of the methylhydrindamines for the resolution of the *dl*-acid, as their salts do not crystallise.

The author gratefully acknowledges the financial assistance, for which he is indebted to the Government Grant Committee of the Royal Society.

UNIVERSITY COLLEGE,
NOTTINGHAM.

XLV.—*The Metallic Picrates.*

By Oswald Silberrad, Ph.D., and Henry Ablett Phillips.

The present investigation was rendered necessary by the numerous discrepancies between the statements of previous workers as to the composition and properties of the metallic picrates. In many instances the older data have had to be corrected.[*]

The metallic salts were, in general, prepared by bringing together picric acid and the carbonate of the metal in question, and evaporating the solution until the crystals appeared on cooling. The chief difficulty encountered is due to the rapidity with which the crystals alter in the air.

Lithium Picrate.

Beamer and Clark obtained the anhydrous salt from alcoholic solution. No hydrated salts appear to have been prepared.

Tetrahydrate, $C_6H_2(NO_2)_3{\cdot}OLi,4H_2O$.—This is obtained by mixing equivalent quantities of lithium carbonate and picric acid and allowing the aqueous solution to evaporate slowly at the ordinary temperature. It crystallises in yellow, prismatic needles, which gradually pass into the monohydrate with separation of water even when kept in atmosphere saturated with moisture:

---

[*] In order to avoid repetition, the references used throughout the present paper are collected together in the following lists, and the authors are referred to only by name in dealing with their work on the various salts:

Welter, *Ann. Chim. Phys.*, 1795, [i], **29**, 301; *Scher. Jour.*, 1800, **3**, 715; Chevreul, *Ann. Chim. Phys.*, 1809, [i], **72**, 113; Hatchett, *Gehl. Ann.*, 1803, **1**, 369; Fourcroy and Vauquelin, *Gehl. Ann.*, 1804, **2**, 231; Liebig, *Schweig. Jour.*, 1827, **49**, 373; *Pogg. Ann.* 1828, **13**, 191; *Ann. Chim. Phys.*, 1827, [ii], **35**, 72; 1828, **37**, 286; Miller, *Pogg. Ann.*, 1835, **36**, 478; Rose, *Pogg. Ann.*, 1840, **49**, 186; Dumas, *Ann. Chim. Phys.*, 1836, [ii], **63**, 265; 1841, **2**, 204; *J. pr. Chem.*, 1841, **24**, 218; *Annalen*, 1841, **39**, 353; Marchand, *J. pr. Chem.*, 1841, **23**, 363; 1844, **32**, 35; *Annalen*, 1843, **48**, 336; 1844, **52**, 345; Schunck, *Annalen*, 1841, **39**, 7; Laurent, *Ann. Chim. Phys.*, 1841, [iii], **3**, 221; *J. pr. Chem.*, 1842, **25**, 427; *Rev. Scient.*, **9**, 26; *Annalen*, 1842, **43**, 219; Kopp, *Ann. Chim. Phys.*, 1845, [iii], **13**, 233; Rieckher, *Arch. Pharm.*, 1845, [ii], **44**, 158; Stenhouse, *Annalen*, 1846, **57**, 88; *J. pr. Chem.*, 1846, **39**, 221; *Journ. Chem. Soc.*, 1868, **21**, 150; Cahours, *Ann. Chim. Phys.*, 1849, [iii], **25**, 26; *J. pr. Chem.*, 1849, **46**, 337; Schabus, *Jahresber.*, 1850, 392; Moretti, compare Gmelin's *Handbuch de Chemie*, 1852, Bd. v, 685; Carey Lea, *Silliman's Journ.*, 1858, **26**, 379; 1860, **30**, 402; 1861, **31**, 78; *Chem. Gaz.*, 1859, 1; *Rep. Chim. pure.*, 1859, **1**, 227; von Rath, *Pogg. Ann.*, 1860, **110**, 114; Kuhlmann, *Annalen*, 1863, **126**, 78; *Bull. Soc. chim.*, 1864, [ii], **1**, 330; *Jahresber.*, 1864, 254; Böttger, *Jahresber. Phys. Vereins. Frankfurt*, 1865, **66**, 56; *Jahresber.*, 1866, 860; Müller, *Zeitsch. für Chem.*, 1865, 189; *Pogg. Ann.*, 1865, **124**, 103; Müller and Stenhouse, *Jahresber.*, 1866, 580; *Quart. Journ. Chem. Soc.*, 1866, **4**, 235; Frisch, *J. pr. Chem.*, 1867, **100**, 229; *Jahresber.*, 1867, 622; Lossen, *Annalen*, 1868, *Suppl.*, **6**, 233; Post and Mehrtens, *Ber.*, 1875, **8**, 1552; Beamer and Clarke, *Ber.*, 1879, **12**, 1068; Reychler, *Ber.*, 1884, **17**, 2264; Tschelzoff, *Ann. Chim. Phys.*, 1886, [vi], **8**, 233; v. Rothenberg, *Ber.*, 1894, **27**, 690; Varet, *Ann. Chim. Phys.*, 1896, [vii], **8**, 130; Hantzsch and Auld, *Ber.*, 1906, **39**, 1105; Cook, *J. Amer. Chem. Soc.*, 1906, **28**, 613.

Found, N = 13·77.

$C_6H_2O_7N_3Li,4H_2O$ requires N = 13·71 per cent.

The *monohydrate*, $C_6H_2(NO_2)_3{\cdot}OLi,H_2O$, is obtained when the tetrahydrate is allowed to stand (preparation I) or, more rapidly when heated to 80° (preparation II). It is also formed when a hot concentrated solution of the salt in water is allowed to cool rapidly (preparation III), and when the anhydrous salt is exposed to air under ordinary conditions (preparation IV) or in an atmosphere 75 per cent. saturated with moisture at 25° (preparation V):

Found, N = (I) 16·90; (II) 16·55; (III) 16·46. H_2O = (I) 6·84; (II) 6·85.

$C_6H_2O_7N_3Li,H_2O$ requires N = 16·64; H_2O = 7·12 per cent.

Loss of weight on exposing tetrahydrate to a temperature of 80°:

Found, (*a*) 17·91; (*b*) 18·07.

$C_6H_2O_7N_3Li,4H_2O$ requires (for a loss of $3H_2O$) 17·60 per cent.

Increase in weight on exposing anhydrous salt to air:

Found, (IV) 7·52; (V) 7·57.

$C_6H_2O_7N_3Li$ requires for $1H_2O$ an increase of 7·66 per cent.

The monohydrate is obtained in dark orange-yellow, rhombic crystals by rapidly cooling a saturated solution, or by allowing the tetrahydrate to stand. When prepared by the other methods, it is a dark yellow powder.

The *anhydrous* salt, $C_6H_2(NO_2)_3{\cdot}OLi$, is obtained by exposing either of the foregoing salts to a temperature of 150°:

Found, N = 16·46.

$C_6H_2O_7N_3Li$ requires N = 16·64 per cent.

The salt is a pale yellow powder which rapidly re-absorbs one molecule of water. It explodes with moderate violence at 318—323°.*

Sodium Picrate.

Previous workers—Liebig, Marchand, Schunck, Rieckher, Cahours.

This salt has generally been thought to be anhydrous; the present work has shown, however, that it crystallises with one molecule of water.

---

* The ignition points of these salts were determined by dropping a small quantity of the anhydrous compound into a tube heated in a metallic bath; the ignition point given is the temperature at which ignition occurs within two seconds of the time of introducing the salt into the tube.

The *monohydrate*, $C_6H_2(NO_2)_3\cdot ONa,H_2O$, crystallises from a hot aqueous solution in small, yellow needles (preparation I).

It is also produced as a yellow powder when the anhydrous salt is exposed to an atmosphere saturated with moisture to the extent of 75 per cent. at 25° (preparation II):

Found, N = (I) 15·76; (I*a*) 15·50; (I*b*) 15·52. H_2O = (I) 6·10; (I*a*) 6·62; (I*b*) 6·51.

$C_6H_2O_7N_3Na,H_2O$ requires N = 15·65; H_2O = 6·69 per cent.

Increase of weight on exposing anhydrous salt to a moist atmosphere (preparation II) = 7·38:

$C_6H_2O_7N_3Na$ requires for $1H_2O$ an increase of 7·17 per cent.

The *anhydrous* salt, $C_6H_2(NO_2)_3\cdot ONa$, is obtained by exposing the monohydrate to a temperature of 150°:

Found, N = 16·80.

$C_6H_2O_7N_3Na$ requires N = 16·77 per cent.

The salt is a pale yellow powder, which explodes feebly at 310—315°.

Potassium Picrate, $C_6H_2(NO_2)_3\cdot OK$.

Previous workers—Welter, Chevreul, Fourcroy and Vauquelin, Liebig, Müller, Dumas, Marchand, Schunck, Laurent, Kopp, Rieckher, Stenhouse, Cahours, Schabus, Frisch, Post and Mehrtens.

The analytical data given by these authors agree, in general, in showing the salt to be anhydrous. This is confirmed by the present work:

Found, N = 15·47.

$C_6H_2O_7N_3K$ requires N = 15·76 per cent.

The salt crystallises from an aqueous solution in yellow, iridescent, prismatic needles. It explodes with moderate violence at 311—316°.

Rubidium Picrate, $C_6H_2(NO_2)_3\cdot ORb$.

This salt has apparently not previously been prepared. It crystallises from water in anhydrous yellow needles:

Found, N = 13·67.

$C_6H_2O_7N_3Rb$ requires N = 13·43 per cent.

It explodes with moderate violence at 300—315°.

Cæsium Picrate, $C_6H_2(NO_2)_3\cdot OCs$.

This salt also has apparently not been previously prepared. It crystallises from water in anhydrous, yellow needles:

Found, N = 11·89.

$C_6H_2O_7N_3Cs$ requires N = 11·67 per cent.

It explodes with moderate violence at 272—277°.

Ammonium Picrate, $C_6H_2(NO_2)_3{\cdot}ONH_4$.

Previous workers—Chevreul, Hatchett, Liebig, Rose, Dumas, Marchand, Schunck, Laurent, Kopp, Cahours, Reychler.

All these authors agree as to the absence of water of crystallisation. Liebig and Cahours both recognise the existence of a yellow and red variety of the salt. These observations have been confirmed in the present work. The salts were obtained by the action of ammonia or ammonium carbonate on picric acid, the latter method being more liable to give rise to the red variety:

Found, N = (red variety) 22·71; (yellow variety) 22·70.

$C_6H_6O_7N_4$ requires N = 22·81 per cent.

On heating, both modifications volatilise without detonation.

Hydrazine Monopicrate, $C_6H_2(NO_2)_3{\cdot}OH,N_2H_4$.

Previous worker—Rothenberg.

This author's analysis agrees with the above formula, which has been confirmed in the present work:

Found, N = 26·70; 26·80.

$C_6H_7O_7N_5$ requires N = 26·87 per cent.

The salt crystallises in orange needles, which, on heating, volatilise without explosion.

Silver Picrate, $C_6H_2(NO_2)_3{\cdot}OAg$.

Previous workers—Chevreul, Liebig, Dumas, Marchand, Schunck, Laurent, Rieckher, Stenhouse, Cahours, Carey Lea, Müller and Stenhouse, Post, and Mehrtens.

The analytical data given points in most cases to the absence of water of crystallisation; in other cases, however (Marchand, Laurent, Post and Mehrtens), the presence of one molecule of water is indicated.

For the present work, silver picrate was obtained by dissolving silver oxide in a hot saturated solution of picric acid. The salt separated on cooling in yellow needles, which contained no water of crystallisation:

Found, N = 12·45.

$C_6H_2O_7N_3Ag$ requires N = 12·53 per cent.

The compound exploded feebly at 336—341°.

Cupric Picrate.

Previous workers—Liebig, Marchand, Müller, Tschelzoff, Carey Lea.

Marchand obtained a mixture of the normal salt with a basic salt, and removed the latter by extraction with alcohol. His analysis of the normal salt corresponded with a pentahydrate which lost four molecules of water at 110°. Müller obtained analytical data which corresponded approximately with $[C_6H_2(NO_2)_3{\cdot}O]_2Cu,10\frac{1}{2}H_2O$.

Tschelzoff described an octahydrate. The present work has not confirmed any of the data.

Undecahydrate, $[C_6H_2(NO_2)_3{\cdot}O]_2Cu,11H_2O$.—This salt is deposited, on cooling, from a hot concentrated solution in large, green prisms:

Found, $N = 11{\cdot}85$. $H_2O = 27{\cdot}84$; $27{\cdot}76$.

$C_{12}H_4O_{14}N_6Cu,11H_2O$ requires $N = 11{\cdot}73$; $H_2O = 27{\cdot}60$ per cent.

The *tetrahydrate*, $[C_6H_2(NO_2)_3{\cdot}O]_2Cu,4H_2O$, is obtained as a greenish-yellow powder when the anhydrous salt is exposed to an atmosphere saturated with moisture to the extent of 75 per cent. at 25°.

The anhydrous salt absorbed $H_2O = 13{\cdot}55$:

$C_{12}H_4O_{14}N_6Cu$ requires increase of $4H_2O = 13{\cdot}86$ per cent.

The *anhydrous* salt, $[C_6H_2(NO_2)_3{\cdot}O]_2Cu$, is obtained by heating either of the foregoing salts to a temperature of 80°:

Found, $N = 15{\cdot}95$.

$C_{12}H_4O_{14}N_6Cu$ requires $N = 16{\cdot}20$ per cent.

The salt is a greenish-yellow powder, which absorbs water from the atmosphere. It explodes violently at 282—287°.

Magnesium Picrate.

Previous workers—Liebig, Marchand, Tschelzoff.

Marchand's data led him to regard the salt as a pentahydrate, whilst Tschelzoff considered it an octahydrate.

The present work does not confirm these data.

Nonahydrate, $[C_6H_2(NO_2)_3{\cdot}O]_2Mg,9H_2O$.—This salt crystallises from a hot concentrated solution in silky, yellow needles:

Found, $N = 13{\cdot}32$; $13{\cdot}39$.

$C_{12}H_4O_{14}Mg,9H_2O$ requires $N = 13{\cdot}11$ per cent.

Hexahydrate, $[C_6H_2(NO_2)_3{\cdot}O]_2Mg,6H_2O$.—This was obtained by exposing the anhydrous salt to the air (preparation I), or to an atmosphere 75 per cent. saturated with moisture at 25° (preparation II). The increase in weight corresponds with the addition of $6H_2O$.

Increase in weight on exposing anhydrous salt to air = (I) 22·39.

Increase in weight on exposing anhydrous salt to an atmosphere 75 per cent. saturated with moisture at 25° = 22·40:

$C_{12}H_4O_{14}N_6Mg$ requires increase of $6H_2O$ = 22·49 per cent.

The *dihydrate*, $[C_6H_2(NO_2)_3{\cdot}O]_2Mg,2H_2O$, is obtained when the nonahydrate is heated to a temperature of 80°:

Found, N = (I) 16·35; (II) 16·42. H_2O = (I) 7·09.

$C_{12}H_4O_{14}N_6Mg,2H_2O$ requires N = 16·30; H_2O = 6·97 per cent.

Loss of weight on exposing nonahydrate to a temperature of 80° = 19·33:

$C_{12}H_4O_{14}N_6Mg,9H_2O$ requires $7H_2O$ = 19·62 per cent.

The *anhydrous* salt, $[C_6H_2(NO_2)_3{\cdot}O]_2Mg$, is obtained when any of the above hydrates are heated to a temperature of 150°:

Found, N = 17·32.

$C_{12}H_4O_{14}N_6Mg$ requires N = 17·53 per cent.

This salt explodes very feebly at 367—372°.

Calcium Picrate.

Previous workers.—Chevreul, Liebig, Marchand, Tschelzoff.

According to Marchand, the crystalline salt is a pentahydrate; Tschelzoff gives a formula containing $6H_2O$. The present work shows that the crystals consist of a decahydrate.

Decahydrate, $[C_6H_2(NO_2)_3{\cdot}O]_2Ca,10H_2O$, crystallises from a hot concentrated solution, on cooling, in yellow plates:

Found, N = (I) 12·59; (II) 12·37. H_2O = (I) 26·95; (II) 26·03.

$C_{12}H_4O_{14}N_6Ca,10H_2O$ requires N = 12·45; H_2O = 26·63 per cent.

Pentahydrate?, $[C_6H_2(NO_2)_3{\cdot}O]_2Ca,5H_2O$, appears to be formed when the anhydrous salt is exposed to the air (preparation I) or to an atmosphere 75 per cent. saturated with moisture at 25° (preparation II).

Increase in weight of anhydrous salt: (I) 17·50, 17·07; (II) 17·00:

$[C_6H_2(NO_2)_3{\cdot}O]_2Ca$ requires for $5H_2O$ an increase of 18·15 per cent.

The *anhydrous* salt is produced when the decahydrate is heated to 80°:

Found, N = 16·56; 16·57.

$C_{12}H_4O_{14}N_6Ca$ requires N = 16·97 per cent.

It is a yellow powder, which explodes violently at 323—328°.

Strontium Picrate.

Previous workers—Chevreul, Marchand, Rieckher, Cahours, von Rath, Tschelzoff.

Marchand and von Rath found the salt to contain $5H_2O$; the former showed that one molecule of water remained on heating to 150°. Tschelzoff found $6H_2O$, and Rieckher gives data which would correspond with $6H_2O$ if the salt be assumed to lose all its water at 130°. The present work confirms Marchand's results.

Pentahydrate, $[C_6H_2(NO_2)\cdot O]_2Sr,5H_2O$, crystallises in yellow needles from a hot concentrated solution (preparation I); it is also formed when the monohydrate is exposed to the air (preparation II), or to an atmosphere 75 per cent. saturated with moisture at 25° (preparation III):

Found, N = (I) 13·29; 13·48.

$C_{12}H_4O_{14}N_6Sr,5H_2O$ requires N = 13·29 per cent.

Increase in weight on exposing monohydrate to air = (II) 13·00; (III) 13·18:

$C_{12}H_4O_{14}N_6Sr,H_2O$ requires for an addition of $4H_2O$ an increase of 12·82 per cent.

The *monohydrate*, $[C_6H_2(NO_2)_3\cdot O]_2Sr,H_2O$, is obtained when the pentahydrate is exposed to a temperature of 80°:

Found, N = 14·70; 14·70.

$C_{12}H_4O_{14}N_6Sr,H_2O$ requires N = 14·99 per cent.

Loss of weight on heating pentahydrate = 11·79; 11·75.

$C_{12}H_4O_{14}N_6Sr,5H_2O$ requires (for a loss of $4H_2O$) 11·37 per cent.

The salt is a yellow powder, which explodes fairly violently at 340—345°.

The *anhydrous* salt, $[C_6H_2(NO_2)_3\cdot O]_2Sr$, is obtained when either of the foregoing salts is heated to 200°, but even at this temperature the water is expelled with difficulty:

Found, N = 15·40; 15·40.

$C_{12}H_4O_{14}N_6Sr$ requires N = 15·49 per cent.

Barium Picrate.

Previous workers—Chevreul, Liebig, Dumas, Marchand, Schunck, Laurent, Rieckher, Cahours, Carey Lea, Post and Mehrtens, Tschelzoff, Cook.

The analytical data show considerable discrepancies; those of Liebig correspond with $2\frac{1}{2}$—$4\frac{1}{2}H_2O$. Post and Mehrtens found $4H_2O$; Marchand and Rieckher, $5H_2O$; Laurent and Tschelzoff, $6H_2O$; Cook, $3H_2O$ and $5H_2O$, and Marchand and Tschelzoff also obtained evidence of the formation of a monohydrate on heating. The present work confirms the existence of only one definite hydrate.

The *pentahydrate*, $[C_6H_2(NO_2)_3\cdot O]_2Ba,5H_2O$, crystallises from a concentrated aqueous solution in yellow, prismatic needles:

Found, N = 12·14. H_2O = 13·23.

$C_{12}H_4O_{14}N_6Ba,5H_2O$ requires N = 12·29 ; H_2O = 13·17 per cent.

The *an hdrous* salt, $[C_6H_2(NO_2)_3{\cdot}O]_2Ba$, is obtained when the pentahydrate is exposed to a temperature of 80°:

Found, N = 14·09.

$C_{12}H_4O_{14}N_6Ba$ requires N = 14·19 per cent.

The salt is a yellow powder, which explodes with moderate violence at 333—337°. On being exposed to the air or to an atmosphere 75 per cent. saturated with moisture at 25°, an intermediate hydrate appears to be formed; thus the increase of weight corresponded with the addition of:

In the air of the laboratory, (I) $4{\cdot}5H_2O$; (II) $4{\cdot}65H_2O$.

In moist atmosphere (75 per cent. saturated at 25°), $4{\cdot}6H_2O$.

Zinc Picrate.

Previous workers—Marchand, Carey Lea, Müller, Tschelzoff.

Marchand believed he obtained salts containing $8H_2O$, $5H_2O$, $2H_2O$, and H_2O, but the analytical data show great discrepancies.

Tschelzoff's zinc determination points to the presence of $9H_2O$, but the loss of weight corresponds more nearly with $8H_2O$. Müller investigated the double picrate of zinc and sodium. The present work has shown the existence of salts containing $9H_2O$, $6H_2O$, and $2H_2O$.

Nonahydrate, $[C_6H_2(NO_2)_3{\cdot}O]_2Zn,9H_2O$.—This separates from the concentrated solution in yellow, prismatic needles:

Found, N = 12·41 ; 12·40.

$C_{12}H_4O_{14}N_6Zn,9H_2O$ requires N = 12·32 per cent.

Hexahydrate, $[C_6H_2(NO_2)_3{\cdot}O]_2Zn,6H_2O$.—This was formed by exposing the anhydride to an atmosphere 75 per cent. saturated with moisture.

Increase in weight of anhydrous salt = 20·50:

$C_{12}H_4O_{14}N_6Zn$ requires the addition of $6H_2O$ = 20·72 per cent.

In the air of the laboratory, the amount of moisture absorbed was rather less (5·4 and 5·6 molecules).

The *dihydrate*, $[C_6H_2(NO_2)_3{\cdot}O]_2Zn,2H_2O$, is formed when the nonahydrate is heated to 80°:

Found, N = (I) 15·11 ; (II) 15·04.

$C_{12}H_4O_{14}N_6Zn,2H_2O$ requires N = 15·1.

Loss of weight on exposing nonahydrate to a temperature of 80° = 18·54:

$C_{12}H_4O_{14}N_6Zn,9H_2O$ requires (for a loss of $7H_2O$) 18·44 per cent.

The *anhydrous* salt, $[C_6H_2(NO_2)_3\cdot O]_2Zn$, is produced when any of the hydrates are heated to 150°:

Found, $N = 15{\cdot}93$.

$C_{12}H_4O_{14}N_6Zn$ requires $N = 16{\cdot}15$ per cent.

It is a brownish-yellow powder, which explodes violently at 350—355°.

Cadmium Picrate.

Previous workers—Müller, Carey Lea.

The analysis given by Müller corresponds with a heptahydrate. This has been confirmed in the present work.

Heptahydrate, $[C_6H_2(NO_2)_3\cdot O]_2Cd,7H_2O$.—This salt was obtained from hot concentrated solution in the form of yellow, hexagonal plates:

Found, $N = $ (I) 12·13; (II) 11·97. $H_2O = $ (I) 18·29; (II) 17·93.

$C_{12}H_4O_{14}N_6Cd,7H_2O$ requires $N = 12{\cdot}12$; $H_2O = 18{\cdot}15$ per cent.

The *pentahydrate*, $[C_6H_2(NO_2)_3\cdot O]_2Cd,5H_2O$, is formed when the anhydrous salt is exposed to an atmosphere 75 per cent. saturated with moisture at 25°.

Increase in weight = 16·14:

$[C_6H_2(NO_2)_3\cdot O]_2Cd$ requires for $5H_2O$ an increase = 15·84 per cent.

The same result was not obtained when the anhydrous salt was exposed to the air of the laboratory, approximately 4 molecules only of water being absorbed.

The *anhydrous* salt, $[C_6H_2(NO_2)_3\cdot O]_2Cd$, is formed when the heptahydrate is exposed to 80°:

Found, $N = 14{\cdot}61$.

$C_{12}H_4O_{14}N_6Cd$ requires $N = 14{\cdot}81$ per cent.

It is a yellow powder, which explodes violently at 336—341°.

Mercuric Picrate.

Liebig and Moretti described a mercurous picrate; Chevreul, Varet, Carey Lea, and Hantzsch and Auld have described mercuric salts. Varet and Hantzsch and Auld give directions for the preparation of a tetrahydrated normal mercuric salt by digesting freshly-precipitated mercuric oxide with an aqueous solution of picric acid at 80°.

In the present investigation, all attempts to prepare this substance by repeating this work gave rise to the basic compound described below.

Hexahydrate, $[C_6H_2(NO_2)_3\cdot O]_2Hg,Hg(OH)_2,6H_2O$.—This compound was obtained by three slightly different methods:

(1) By keeping a well-stirred mixture of picric acid, in excess (46 grams in two litres of water), and freshly-precipitated mercuric oxide

(21 grams) at a temperature of 80° for forty-eight hours. On cooling, the salt separated as beautiful orange-yellow needles.

(2) By warming a similar mixture for a few hours only. In this case, the salt, which was precisely similar in appearance, was much contaminated with free picric acid, which was, however, readily removed by crystallisation from hot water.

(3) By boiling a similar mixture for seven hours after maintaining it at 80° for forty-eight hours. On analysis:

Found, N = (I) 8·46; (II) 8·44; (III) 8·50. H_2O = (I) 10·25.

$C_{12}H_{18}O_{22}N_6Hg_2$ requires N = 8·44; H_2O = 10·82 per cent.

The compound forms beautiful orange needles, which change to a pale yellow colour on losing the water of crystallisation. On warming with water, a residue of mercuric oxide is obtained, and on concentrating the solution the hydrated basic salt again separates, picric acid being left in solution.

The *anhydrous* salt, $[C_6H_2(NO_2)_3 \cdot O]_2Hg,Hg(OH)_2$, is obtained by exposing the finely-powdered hexahydrate over sulphuric acid in a vacuum:

Found, N = 9·46. H_2O = 44·82.

$C_{12}H_6O_{16}N_6Hg_2$ requires N = 9·46; H_2O = 44·93 per cent.

The salt is a pale yellow powder, which volatilises without explosion on heating.

Aluminium Picrate.

Previous workers—Carey Lea, Müller, Moretti.

Müller gives analyses which correspond with a basic salt,

$$[C_6H_2(NO_2)_3 \cdot O]_2AlOH,7H_2O,$$

whilst Lea gives no analytical data.

Hexadecahydrate, $[C_6H_2(NO_2)_3 \cdot O]_3Al,16H_2O$.—This was prepared by digesting freshly-precipitated aluminium hydroxide with an aqueous solution of picric acid for several days, and concentrating the filtrate; on cooling, the salt was deposited in pale yellow needles (preparation I). It may also be obtained by exposing the tetrahydrate to an atmosphere 75 per cent. saturated with moisture at 25° (preparation II):

Found, (I) N = 12·81.

$C_{18}H_6O_{21}N_9Al,16H_2O$ requires N = 12·64 per cent.

Increase of weight on exposing the tetrahydrate to moist air = (II) 27·84:

$C_{18}H_6O_{21}N_9Al,4H_2O$ requires increase of $12H_2O$ = 27·59 per cent.

A similar result is not obtained on exposing the tetrahydrate to the air of the laboratory, only approximately 10·7 molecules of water being absorbed.

The *tetrahydrate*, $[C_6H_2(NO_2)_3{\cdot}O]_3Al,4H_2O$, is obtained from the hexadecahydrate by heating to 80°:

Found, N = 16·01; 16·07.

$C_{18}H_6O_{21}N_9Al,4H_2O$ requires N = 16·13 per cent.

Loss of weight on exposing the hexadecahydrate to a temperature of 80° = 22·33; 22·56:

$C_{18}H_6O_{21}N_9Al,16H_2O$ requires loss (of $12H_2O$) = 21·92 per cent.

The tetrahydrate thus obtained is a yellow powder, which on heating decomposes without explosion.

Thallium Picrate, $C_6H_2(NO_2)_3{\cdot}OTl$.

Previous workers—Kuhlmann, Böttger.

No analytical data are given by these authors. In the present work, thallium carbonate was dissolved in aqueous picric acid, and the filtrate concentrated. The anhydrous salt crystallised in silky, yellow needles. No loss of weight occurred on heating:

Found, N = 9·68.

$C_6H_2O_7N_3Tl$ requires N = 9·75 per cent.

The salt explodes feebly at 273—275°.

Zirconium Picrate, $[C_6H_2(NO_2)_3{\cdot}O]_4Zr$.

This salt has apparently not been previously prepared. It was obtained from zirconium carbonate and picric acid, and crystallises in anhydrous, silky, yellow needles:

Found, N = 16·67.

$C_{24}H_8O_{28}N_{12}Zr$ requires N = 16·80 per cent.

The salt suffered practically no loss in weight on heating; it exploded freely at 317—322°.

Cerium Picrate.

This salt has apparently not been previously prepared. In the present work, it was obtained from cerium carbonate and picric acid.

Undecahydrate, $[C_6H_2(NO_2)_3{\cdot}O]_3Ce,11H_2O$, crystallises from a concentrated aqueous solution (preparation I), and can also be obtained by exposing the anhydrous salt to air (preparation II) or to an atmosphere 75 per cent. saturated with moisture at 25° (preparation (III):

Found, N = 12·32.

$C_{18}H_6O_{21}N_9Ce,11H_2O$ requires N = 12·35 per cent.

Increase in weight on exposing anhydrous salt to air = (II) 24·32; (III) 24·60:

$C_{18}H_6O_{21}N_9Ce$ requires for $11H_2O$ an increase of 24·03 per cent.

The salt separates from a concentrated aqueous solution in amber-coloured, flat, prismatic crystals. By either of the other methods, it is obtained as a brown powder.

The *trihydrate*, $[C_6H_2(NO_2)_3\cdot O]_3Ce,3H_2O$, is obtained by heating the undecahydrate to 80°:

Found, N = (I) 14·30; (II) 14·23. H_2O = (I) 6·69; (II) 6·92.

$C_{18}H_6O_{21}N_9Ce,3H_2O$ requires N = 14·38; H_2O = 6·22 per cent.

Loss of weight on heating undecahydrate to 80° = 14·04; 14·11:

$C_{18}H_6O_{21}N_9Ce,11H_2O$ requires loss (of $8H_2O$) = 14·09 per cent.

It is a brown powder, which absorbs moisture from the air.

The *anhydrous* salt, $[C_6H_2(NO_2)_3\cdot O]_3Ce$, is obtained when either the undecahydrate or trihydrate is heated to 150°:

Found, N = 15·22.

$C_{18}H_6O_{21}N_9Ce$ requires N = 15·29 per cent.

The salt is a brown powder, which explodes violently at 306—313°.

Lead Picrate.

Previous workers—Chevreul, Liebig, Marchand, Laurent, Kopp, Rieckher, Post and Mehrtens, Tschelzoff.

The analytical data vary very considerably; they correspond with 1 to 5 molecules of water of crystallisation. Various basic salts are also described.

Tetrahydrate, $[C_6H_2(NO_2)_3\cdot O]_2Pb,4H_2O$.—Picric acid was treated with lead carbonate, and the salt obtained in the form of silky, yellow needles:

Found, N = 11·46.

$C_{18}H_4O_{14}N_6Pb,4H_2O$ requires N = 11·46 per cent.

The *monohydrate*, $[C_6H_2(NO_2)_3\cdot O]_2Pb,H_2O$, results when the tetrahydrate is retained at 80° for some time (preparation I), and also when the anhydrous salt is exposed to air (preparation II):

Found, N = (I) 12·56. H_2O = 2·77; 2·71.

$C_{12}H_4O_{14}N_6Pb,H_2O$ requires N = 12·37; H_2O = 2·65 per cent.

Increase in weight on exposing anhydrous salt to air (II) = 2·73; 2·71:

$C_{12}H_4O_{14}N_6Pb$ requires for $1H_2O$ an increase of 2·72 per cent.

In an atmosphere 75 per cent. saturated with moisture, 1·3 molecules of water were absorbed.

The *anhydrous* salt, $[C_6H_2(NO_2)_3\cdot O]_2Pb$, is obtained when the tetrahydrate or monohydrate is heated to 150°.

It is a yellow powder, which explodes violently at 270—275°, and differs from all other picrates in being extremely sensitive to shock or friction.

Chromium Picrate.

Carey Lea describes a chromium-ammonium compound, but chromium picrate has apparently not been prepared.

A basic chromium salt, corresponding approximately with the composition $[C_6H_2(NO)_3\cdot O]_3Cr,2C_6H_2(NO_2)_3\cdot O\cdot CrO,27H_2O$, is obtained by mixing equivalent quantities of barium picrate and chromium sulphate and evaporating the filtrate in a vacuum over sulphuric acid.

The salt separates in green crystals:

Found, Cr = (I) 8·30; (II) 8·61. N = (I) 11·38.

$C_{30}H_{10}O_{36}N_{15}Cr,27H_2O$ requires Cr = 8·61; N = 11·60 per cent.

A salt of the composition

$$[C_6H_2(NO_2)_3\cdot O]_3Cr,2C_6H_2(NO_2)_3\cdot O\cdot CrO,9H_2O$$

is produced when the salt just described is heated to 80°.

Loss of weight on heating to 80° = (I) 18·21; (II) 18·11:

$C_{30}H_{10}O_{36}N_{15}Cr,27H_2O$ requires for loss (of $18H_2O$) = 17·86 per cent.

The *anhydrous* salt, $[C_6H_2(NO_2)_3\cdot O]_3Cr,2C_6H_2(NO_2)_3\cdot O\cdot CrO$, is produced when the foregoing salt is heated to 150°.

Loss of weight on heating to 150° = (I) 10·16; (II) = 10·49.

$C_{30}H_{10}O_{36}N_{15}Cr,9H_2O$ requires loss (of $9H_2O$) = 10·88 per cent.

Manganese Picrate.

Previous workers—Marchand, Müller, Carey Lea.

Marchand obtained an octahydrate which readily lost three molecules of water; Müller found only a pentahydrate. The present work shows the existence of the octahydrate and a trihydrate, but renders the formation of a pentahydrate highly improbable.

The *octahydrate*, $[C_6H_2(NO_2)_3\cdot O]_2Mn,8H_2O$, separates in yellow prisms from a hot concentrated solution (preparation I).

It is also obtained when the anhydrous salt is exposed to the air (preparation II) or to an atmosphere 75 per cent. saturated at 25° (preparation III):

Found, N = (I) 12·90; 13·02.

$C_{12}H_4O_{14}N_6Mn,8H_2O$ requires N = 12·85 per cent.

Increase in weight on exposing anhydrous salt in air = (II) 27·96; (III) 27·52:

$C_{12}H_4O_{14}N_6Mn$ requires for $8H_2O$ an increase of 28·18 per cent.

The *trihydrate*, $[C_6H_2(NO_2)_3\cdot O]_2Mn,3H_2O$, is produced when the octahydrate is heated to 80°:

Found, N = 15·11. H_2O = 9·44.

$C_{12}H_4O_{14}N_6,3H_2O$ requires N = 14·90; H_2O = 9·56 per cent.

Loss of weight on heating octahydrate to 80° = 13·77; 13·80; 14·02:

$C_{12}H_4O_{14}N_6Mn,8H_2O$ requires loss (of $5H_2O$) = 13·74 per cent.

The *anhydrous* salt, $[C_6H_2(NO_2)_3\cdot O]_2Mn$, is produced when either the octa- or tri-hydrate is heated to 150°.

It is a yellow powder, which explodes with violence at 325—330°.

Ferrous Picrate.

Previous workers—Müller, Carey Lea.

The analysis given by Müller corresponds approximately with a pentahydrate. The present work has not confirmed this, but an octahydrate has been obtained.

Octahydrate, $[C_6H_2(NO_2)_3\cdot O]_2Fe,8H_2O$.—Hot concentrated solutions of ferrous sulphate and barium picrate are mixed and filtered. The ferrous picrate separates from the filtrate, on cooling, in yellow, hexagonal prisms:

Found, N = 12·81. H_2O = 21·72; 21·64; 21·91.

$C_{12}H_4O_{14}N_6Fe,8H_2O$ requires N = 12·84; H_2O = 21·96 per cent.

The crystallised salt is bright yellow, but becomes dark green directly it begins to lose water.

The *anhydrous* salt, $[C_6H_2(NO_2)_3\cdot O]_2Fe$, is obtained when the octahydrate is exposed in a vacuum desiccator over concentrated sulphuric acid:

Found, N = 16·18.

$C_{12}H_4O_{14}N_6Fe$ requires N = 16·45 per cent.

The *anhydrous* salt is a dark green powder, which explodes feebly at 315—320°. On exposure to the air, it absorbs from 3 to 4 molecules of water.

Attempts to prepare ferric picrate were without result; no precipitate was found under the conditions described by Moretti.

Cobalt Picrate.

Previous workers—Marchand, Müller, Carey Lea.

Marchand obtained analytical data corresponding with a pentahydrate. This is not confirmed by the present work. The hydrates obtained contain 9½, 6, and 2 molecules of water, and are strictly analogous to the nickel salts.

Hydrate, $[C_6H_2(NO_2)_3\cdot O]_2Co,9\frac{1}{2}H_2O$.—This is deposited on allowing a hot solution containing 10 grams of the anhydrous salt in 20 c.c. of water to cool:

Found, N = 12·53.

$C_{12}H_4O_{14}N_6Co,9\frac{1}{2}H_2O$ requires N = 12·27 per cent.

The salt crystallises in brown needles.

Hexahydrate, $[C_6H_2(NO_2)_3{\cdot}O]_2Co,6H_2O$.—This crystallises on cooling from a hot solution containing 10 grams of the anhydrous salt in 15 c.c. of water (preparation I).

It is also produced when the anhydrous salt is exposed to air (preparation II) or to an atmosphere 75 per cent. saturated at 25° (preparation III).

Increase in weight on exposing anhydrous salt to air = (II) 21·07; (III) 21·03.

$C_{12}H_4O_{14}N_6Co$ requires for $6H_2O$ an increase = 20·98 per cent.

When obtained as in preparation (I), the salt crystallises in brown laminæ; by either of the other methods, it is a brown powder.

The *dihydrate*, $[C_6H_2(NO_2)_3{\cdot}O]_2Co,2H_2O$, is formed when either of the above hydrates are heated to 80°.

Dihydrate from 9½ hydrate: Found, N = 15·32. H_2O = 6·10.

Dihydrate from hexahydrate: Found, N = 15·20. H_2O = 6·00.

$C_{12}H_4O_{14}N_6Co,2H_2O$ requires N = 15·28; H_2O = 6·54 per cent.

Loss in weight on heating 9½ hydrate to 80° = 19·43; 19·39; 19·38:

$C_{12}H_4O_{14}N_6Co,9\frac{1}{2}H_2O$ requires a loss (of $7\frac{1}{2}H_2O$) = 19·68 per cent.

Loss of weight on heating hexahydrate to 80° = 11·84; 11·62:

$C_{12}H_4O_{14}N_6Co,6H_2O$ requires a loss (of $4H_2O$) = 11·59 per cent.

Obtained by either method the salt is a brown powder.

The *anhydrous* salt, $[C_6H_2(NO_2)_3{\cdot}O]_2Co$, is obtained when any of the above hydrates are heated to 150°.

It is a brown powder, which explodes with moderate violence at 320—325°.

Nickel Picrate.

Previous workers—Marchand, Müller, Carey Lea.

Marchand describes an octahydrate, a pentahydrate, and a monohydrate. The present work has not confirmed the existence of any of these salts.

Hydrate, $[C_6H_2(NO_2)_3{\cdot}O]_2Ni,9\frac{1}{2}H_2O$.—This crystallises in green needles when a hot solution containing 10 grams of the anhydrous salt in 20 c.c. of water is allowed to cool:

Found, N = 12·47.

$C_{12}H_4O_{14}N_6Ni,9\frac{1}{2}H_2O$ requires N = 12·28 per cent.

Hexahydrate, $[C_6H_2(NO_2)_3{\cdot}O]_2Ni,6H_2O$.—This crystallises in green laminæ when a hot solution containing 10 grams of anhydrous salt in 15 c.c. of water is allowed to cool (preparation I).

It is also produced when the anhydrous salt is exposed to air (preparation II) or to an atmosphere 75 per cent. saturated at 25° (preparation III).

Increase in weight on exposing anhydrous salt to air = (I) 20·24; 20·90; (II) 20·24.

$C_{12}H_4O_{14}N_6$ requires for $6H_2O$ an increase of 20·99 per cent.

Obtained by preparation I, the salt crystallises in the form of green laminæ; by either of the other methods, it is a green powder.

The *dihydrate*, $[C_6H_2(NO_2)_3\cdot O]_2Ni,2H_2O$, is obtained from either of the above hydrates on heating to 80°.

Dihydrate from $9\frac{1}{2}$ hydrate: Found, N = 15·26.

Dihydrate from hexahydrate: Found, N = 15·21. H_2O = 6·70:

$C_{12}H_4O_{14}N_6Ni,2H_2O$ requires N = 15·29; H_2O = 6·54 per cent.

Loss in weight on heating $9\frac{1}{2}$ hydrate to 80° = 19·90; 20·09:

$C_{12}H_4O_{14}N_6Ni,9\frac{1}{2}H_2O$ requires a loss (of $7\frac{1}{2}$ H_2O) = 19·69 per cent.

Obtained by either method, the salt is a green powder.

The *anhydrous* salt, $[C_6H_2(NO_2)_3\cdot O]_2Ni$, is obtained when any of the above hydrates are heated to 150°. It is a green powder, which explodes with moderate violence at 335—340°.

Our thanks are due to the Director of Artillery, the Ordnance Research Board, and the Explosives Committee for permission to publish these results, and also to Messrs. C. S. Roy, H. J. Merriman, and F. W. Myers for assistance in the work.

CHEMICAL RESEARCH LABORATORIES,
ROYAL ARSENAL, WOOLWICH.

XLVI.—*Brazilin and Haematoxylin. Part VIII.* Synthesis of Brazilinic Acid, the Lactones of Dihydrobrazilinic and Dihydrohaematoxylinic Acids, Anhydrobrazilic Acid, &c. The Constitution of Brazilin, Haematoxylin, and their Derivatives.*

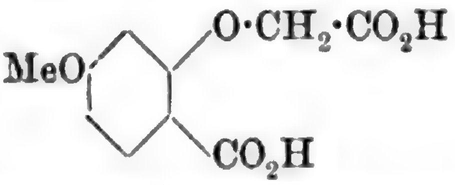
By WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON.

IN investigating the alkaloids and other highly complex natural products, experience has shown that the method most likely to yield information directly bearing on the question of constitution is that of exhaustively studying the degradation products which such substances yield when they are submitted to oxidation under a variety of conditions. During the course of the long and difficult investigation of brazilin and hæmatoxylin, it has been clearly demonstrated that this method of degradation, applied under suitable conditions, yields, in this case also, results of the first importance, and, indeed, our present knowledge of the constitution of these substances is entirely based on the results which were obtained in this way. Since brazilin contains three and hæmatoxylin four phenolic hydroxyl groups, it was necessary to protect these before investigating the action of oxidising agents, and this was done in the usual way by methylation, either with methyl iodide or, better, with methyl sulphate and potassium hydroxide. The trimethylbrazilin, $C_{16}H_{11}O_2(OMe)_3$, and tetramethylhæmatoxylin, $C_{16}H_{10}O_2(OMe)_4$, thus obtained, were then subjected to oxidation by permanganate or chromic acid, and, as a detailed account of the degradation products formed is to be found in the earlier parts of this research, only those which have a direct bearing on the subsequent development of the subject will be mentioned on the present occasion.

---

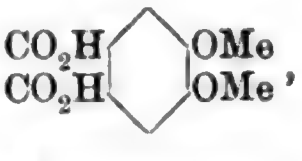
* Part I (Trans., 1901, **79**, 1396), Parts II and III (Trans., 1902, **81**, 221, 235), Parts IV, V, VI (Trans., 1902, **81**, 1008, 1040, 1057), Part VII (Trans., 1907, **91**, 1073).

When trimethylbrazilin is oxidised by permanganate, two acids of great importance are produced, namely:



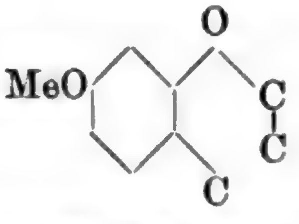
2-Carboxy-5-methoxyphenoxyacetic acid.

and

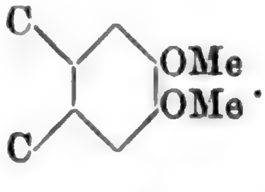


m-Hemipinic acid.

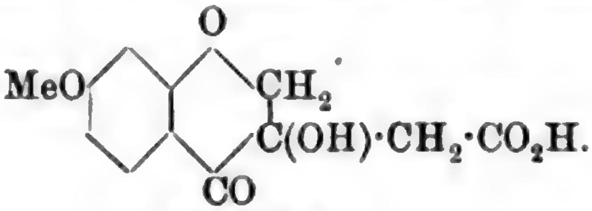
and it was at once recognised (Trans., 1901, **79**, 1401) that the formation of these acids supplied valuable information as to the constitution of trimethylbrazilin, since it was now clear that this substance must be derived not only from a resorcinol, but also from a catechol nucleus, and, further, that the formula of trimethylbrazilin must contain the groupings



and

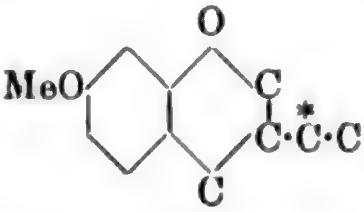


These two residues contain, however, C_{20}, and, as the formula of trimethylbrazilin is $C_{19}H_{20}O_5$, it follows that these residues must be fused together in such a way that one carbon atom is common to both. Perhaps the most important evidence as to the manner in which this fusion takes place is afforded by the study of another acid formed by the oxidation of trimethylbrazilin by permanganate, namely, of brazilic acid. This interesting acid has been most carefully investigated, and it has been conclusively proved by analytical as well as by synthetical experiments (see p. 502) that its constitution must be represented by the formula:

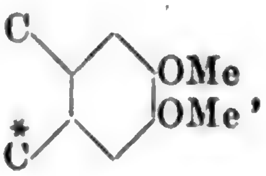


Brazilic acid.

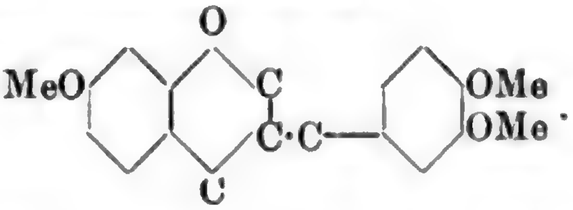
The isolation of this derivative of resorcinol as well as of *m*-hemipinic acid from among the degradation products of trimethylbrazilin clearly proves that the latter contains the groupings



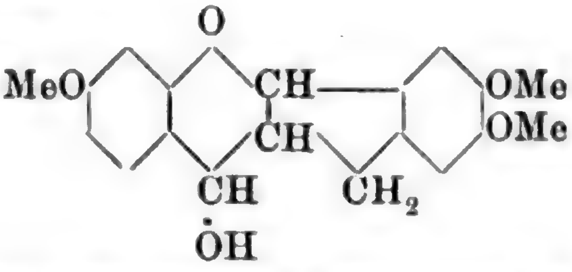
and



and, since these residues must be fused together so that the carbon atoms marked with asterisks are common to both, the skeleton formula for trimethylbrazilin becomes



Many other considerations, which are clearly indicated in the earlier papers, led us to develop this skeleton formula further and to select the expression

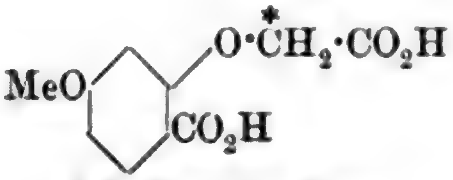


as most probably representing the constitution of trimethylbrazilin (Trans., 1901, **79**, 1401*). This formula appeared to account, in a satisfactory manner, for all the then known reactions and decompositions of this substance, but the evidence on which it was based was, on the other hand, not quite sufficient to allow of its being definitely and unreservedly accepted. During the last few years, facts have gradually accumulated which seemed to suggest that the above formula, although obviously very near the truth, required slight modification. It will not be necessary to enumerate all these facts, as the following example will be sufficient to indicate

* The formula actually given in this reference is that of brazilin itself.

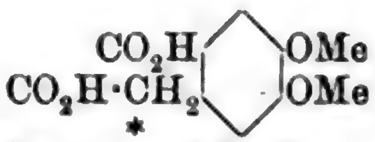
the kind of difficulty which we met with when we attempted to bring some of these facts into harmony with the above formula.

When trimethylbrazilin is oxidised by permanganate, the two acids



2-Carboxy-5-methoxyphenoxyacetic acid.

and

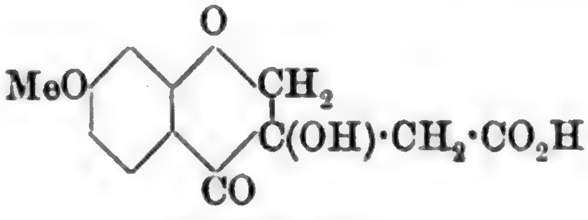


2-Carboxy-4 : 5-dimethoxyphenylacetic acid.

are formed in considerable quantities. Each of these acids contains a $>CH_2$ group (marked with an asterisk), and it will be noticed that brazilic acid (p. 491) also contains the same $>CH_2$ group which is present in carboxymethoxyphenoxyacetic acid.

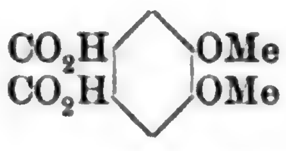
The examination of a large number of cases shows that it is unusual for a $>CH_2$ group to be produced during oxidation with permanganate, and this fact led us to suspect that, in all probability, these two $>CH_2$ groups are contained as such in the correct formula for trimethylbrazilin and occupy, of course, the positions fixed by the formulæ of the degradation products. This condition is not fulfilled in the formula for trimethylbrazilin provisionally adopted (see above), because, although it contains the $>CH_2$ group of carboxydimethoxyphenylacetic acid, it does not contain the $>CH_2$ group of carboxymethoxyphenoxyacetic acid. In order to devise a formula which should satisfy these conditions, we have developed more particularly the following line of argument.

It is clear that the correct formula for trimethylbrazilin must account for the formation of



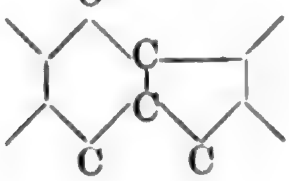
Brazilic acid.

and

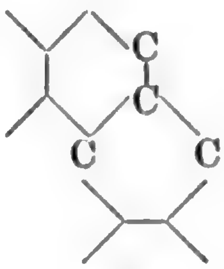


m-Hemipinic acid.

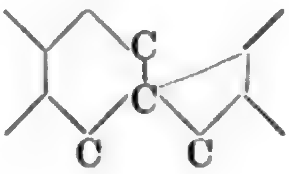
as degradation products. If we confine our attention to the portion of the molecule situated between the two benzene rings, it is evident that there are only three groupings which will account for the formation of the above acids on oxidation:



I.



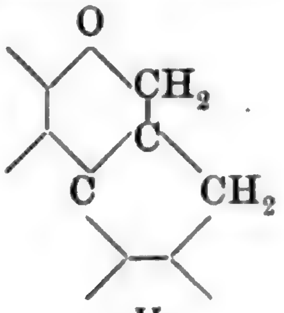
II.



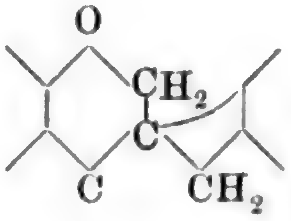
III.

No. I. is the grouping contained in the formula for trimethylbrazilin which has been repeatedly referred to (see p. 491), and which does not allow of the presence of a $>CH_2$ group in the position indicated by brazilic acid and carboxymethoxyphenoxyacetic acid.

It is, however, clear that four atoms of hydrogen may be added to the expressions II. and III., thus:

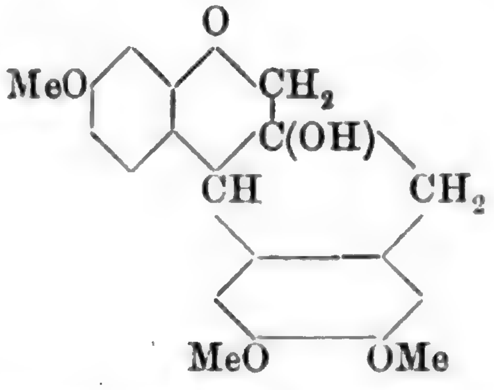


II.



III.

and these expressions then contain the two $>CH_2$ groups of brazilic acid and carboxymethoxyphenoxyacetic acid, on the one hand, and of carboxydimethoxyphenylacetic acid on the other, and are for this reason to be preferred to I. But grouping III. is, obviously, a very unlikely one, and we therefore decided to test the validity of II., the acceptance of which would lead to the formula



as representing the constitution for trimethylbrazilin.*

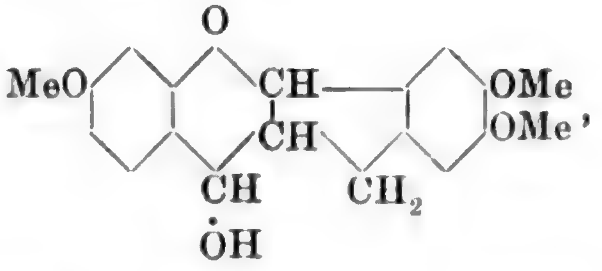
In attacking this difficult problem, we have employed the method of synthesis, and have now succeeded in synthesising all the more important degradation products of trimethylbrazilin with the exception of brazilic acid, so that there can no longer be any doubt as to their constitutions. Of these syntheses, the most important are those of *brazilinic acid* and of the *lactones* of *dihydrobrazilinic* and *dihydrohaematoxylinic acids*, since these, in our opinion, definitely prove the constitutions of both brazilin and hæmatoxylin. Brazilinic acid, $(MeO)_3C_{14}H_7O_2(CO_2H)_2$, is a dibasic acid which is formed in considerable quantities when trimethylbrazilin is oxidised with permanganate (Trans., 1902, **81**, 1014 and 1030).

---

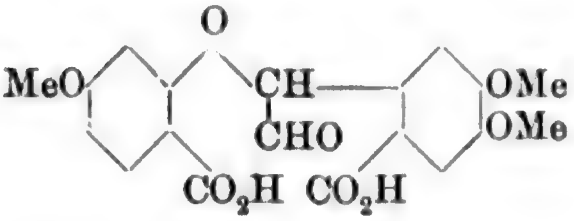
* During the course of an interesting discussion of the degradation products of trimethylbrazilin (described in the present series of papers), Werner and Pfeiffer (*Chem. Zeitsch.*, 1904, **3**, 421) first suggested this formula as possibly representing the constitution of trimethylbrazilin.

It melts at 208°, and one of its most characteristic properties is the fact that, when reduced with sodium amalgam, it is converted by the addition of two atoms of hydrogen and elimination of water into the lactone of dihydrobrazilinic acid (m. p. 227°).

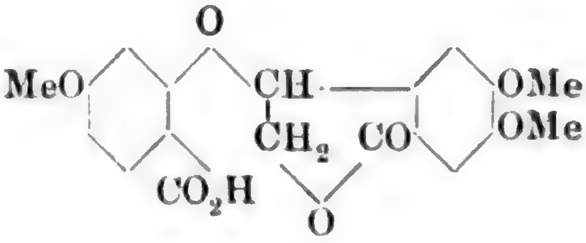
The formula first suggested for trimethylbrazilin, namely:



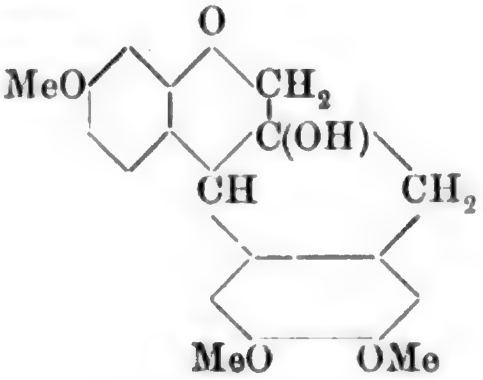
leads to the following expressions for brazilinic acid and the lactone of dihydrobrazilinic acid:



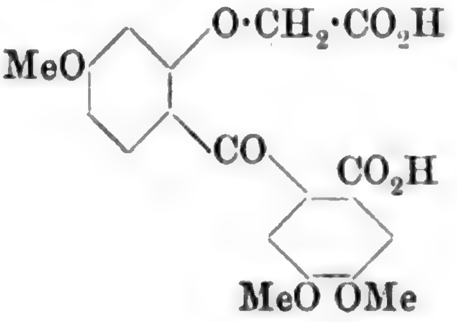
and



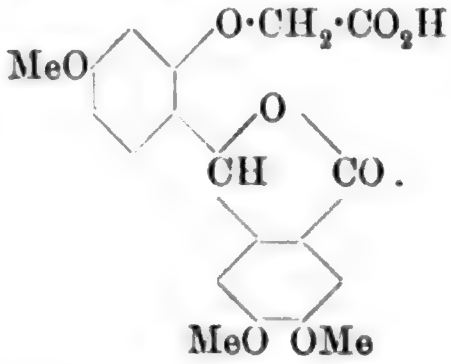
whereas, if the formula



correctly represents trimethylbrazilin, then the corresponding formulæ for brazilinic acid and the lactone of dihydrobrazilinic acid will be:

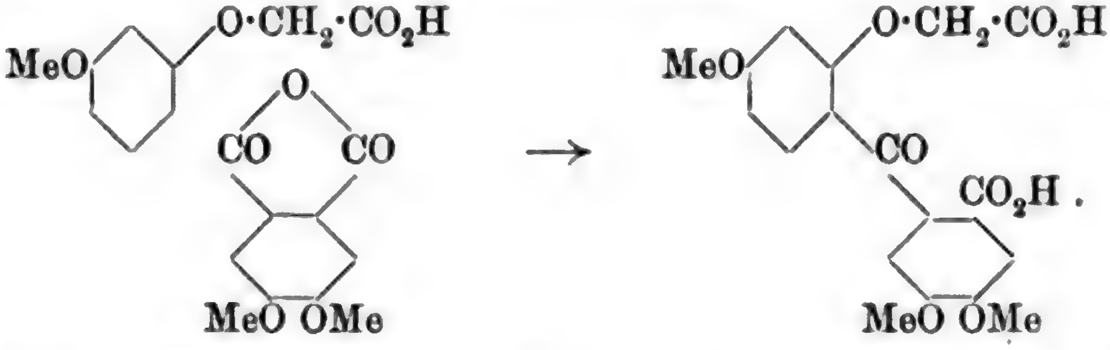


and



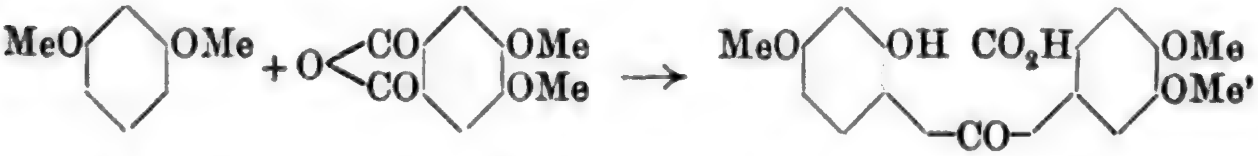
In order to decide this matter definitely, we undertook a series of experiments with the object of synthesising substances having the formulæ last mentioned, and in this we were ultimately successful.

When a mixture of *m*-hemipinic anhydride and ethyl methoxyphenoxyacetate is treated with aluminium chloride, a small quantity of an acid of melting point 208° is formed, which was found by careful comparison to be identical with brazilinic acid (p. 515):

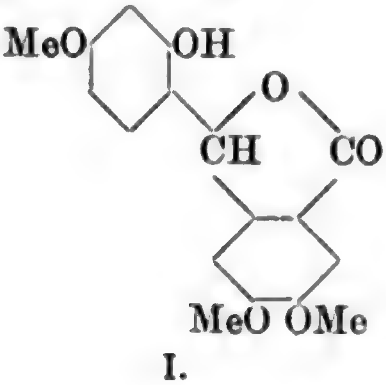


Subsequently the lactone of dihydrobrazilinic acid was synthesised by the following series of reactions (p. 514).

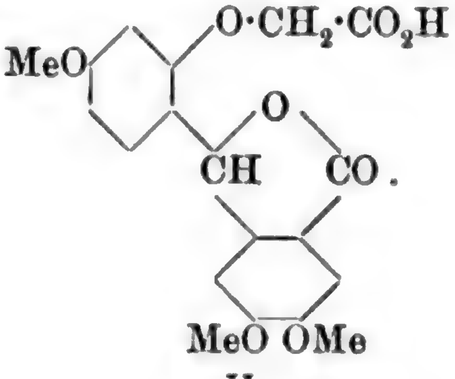
In the first place, *m*-hemipinic anhydride was condensed with resorcinol dimethyl ether in the presence of aluminium chloride, when 2′-*hydroxy*-4:5:4′-*trimethoxy*-2-*benzoylbenzoic acid*[*] was produced:



This ketonic acid was then converted, by reduction with sodium amalgam, into 2-m-*meconyl*-5-*methoxyphenol* (I.):



I.



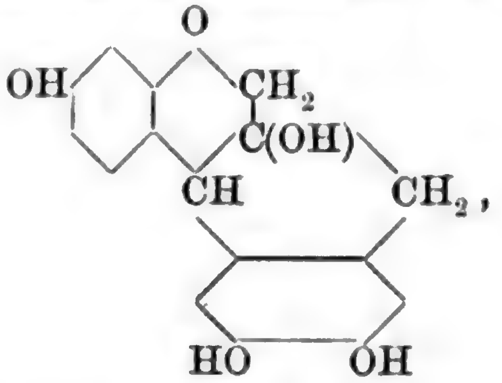
II.

When this lactone is treated with chloroacetic acid and potassium hydroxide, the group $\cdot CH_2\cdot CO_2H$ is introduced in the place of hydrogen of the hydroxyl group, and the substance so produced melts at 227° and is the *lactone* of *dihydrobrazilinic acid*, which consequently must have the constitution II.

These syntheses not only establish the formulæ of brazilinic acid and the lactone of dihydrobrazilinic acid, but they also, at the same time, appear to us to prove conclusively that brazilin must have the constitution represented by the formula:

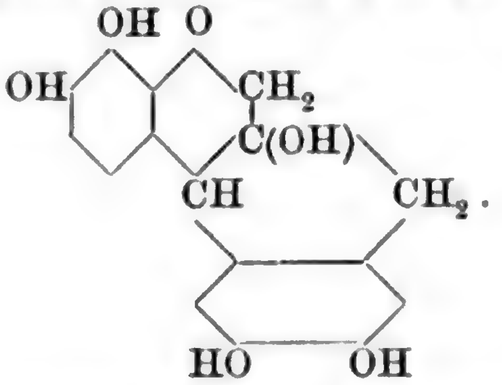
---

[*] The conditions employed were such that hydrolysis of one methoxyl group takes place during the condensation.



since no other constitutional formula, except that containing the hydroxyl group in the place of hydrogen of the >CH group,[*] is capable of yielding brazilinic acid on methylation and oxidation.

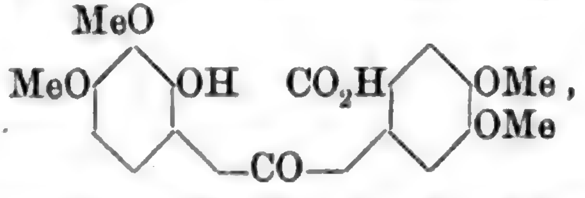
It has long been assumed that hæmatoxylin is analogously constituted to brazilin, and that it contains a pyrogallol residue in the place of the resorcinol residue in brazilin. This view is entirely borne out by the examination of the acids produced during the oxidation of tetramethylhæmatoxylin with permanganate and with chromic acid (Trans., 1902, **81**, 236 and 1057). It follows therefore that the formula for hæmatoxylin is in all probability



In order, however, to obtain further evidence in support of this formula, we decided to attempt the synthesis of the *lactone* of *dihydrohaematoxylinic acid*, a substance which is obtained from tetramethylhæmatoxylin in the same way as the lactone of dihydrobrazilinic acid from trimethylbrazilin (Trans., 1902, **81**, 244), and this was ultimately accomplished in the following manner.

When aluminium chloride reacts with a mixture of pyrogallol trimethyl ether and *m*-hemipinic anhydride, under the conditions given on p. 515, a similar condensation takes place to that already described in the case of the synthesis of the lactone of dihydrobrazilinic acid.

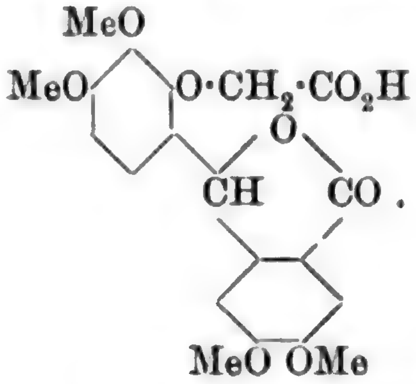
The 2′-*hydroxy*-3′:4′:4:5-*tetramethoxybenzoylbenzoic acid*,



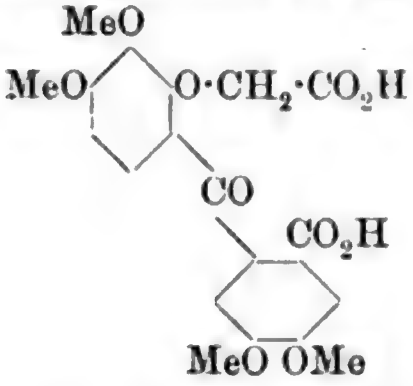
---

[*] That this alternative is impossible will be proved in a future paper on brazilein.

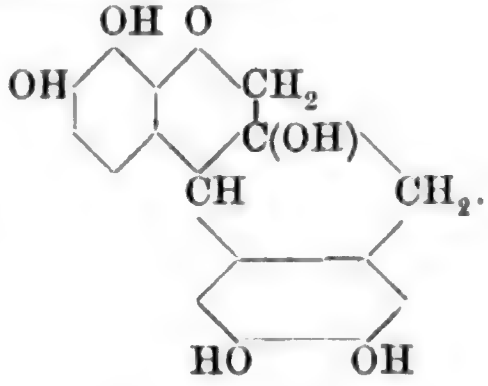
yielded, on reduction and subsequent treatment with chloroacetic acid and potassium hydroxide, a substance which melted at 192—193°, and proved to be the *lactone* of *dihydrohaematoxylinic acid*, which therefore must have the constitutional formula:



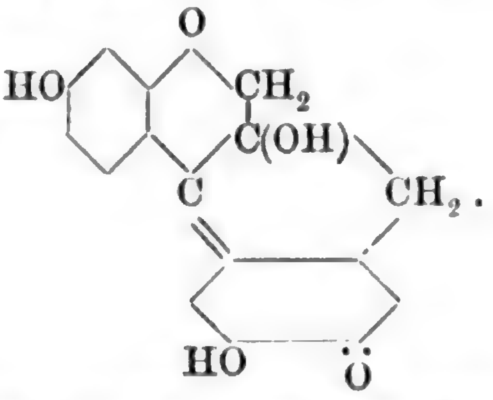
This synthesis also proves that *haematoxylinic acid* and *haematoxylin* must be represented by the formulæ:



and



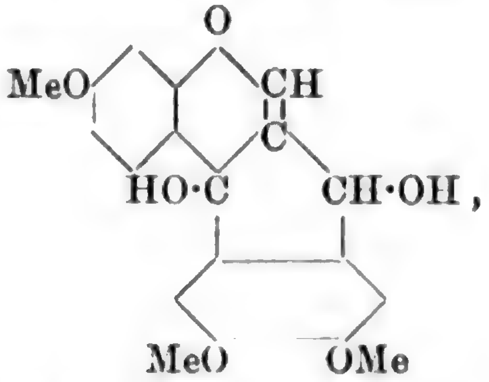
It can readily be shown that the formula adopted above for brazilin accounts in a simple manner for all the decomposition products of this substance, and, in a subsequent paper, dealing with brazilein and its derivatives, which we hope to publish shortly, it will be clearly demonstrated that the constitution of this important oxidation product is readily derived from the formula of brazilin and is to be represented thus:



One of the most puzzling decompositions which trimethylbrazilin undergoes is its conversion into trimethylbrazilone by oxidation with chromic acid (Trans., 1902, **81**, 1040), a change which takes place according to the equation:

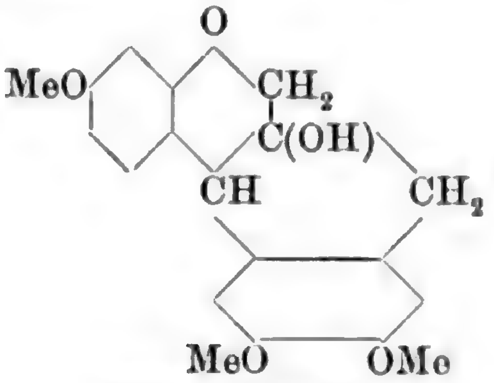
$$(MeO)_3C_{16}H_{11}O_2 + 2O = (MeO)_3C_{16}H_9O_3 + H_2O.$$

Trimethylbrazilone possesses very remarkable properties. It is a ketone which, when treated with potassium hydroxide or dehydrating agents, is converted, with loss of one molecule of water, into *a-anhydrotrimethylbrazilone*, a substance which obviously contains a hydroxyl group, since it readily yields an acetyl compound and a methyl ether. These properties clearly prove that trimethylbrazilone cannot possess the constitution

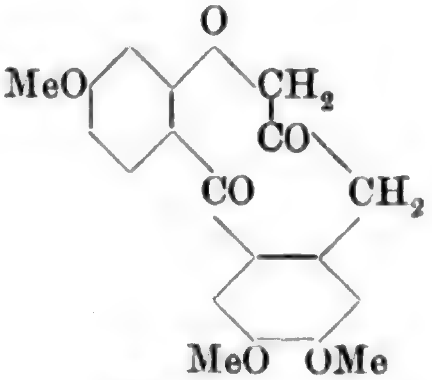


which Werner and Pfeiffer (*Chem. Zeitsch.*, 1904, **3**, 421) have suggested, and which they derived directly from the formula of trimethylbrazilin by oxidation and elimination of water. A very careful consideration of the properties of trimethylbrazilone has led us to the conclusion that this substance cannot be directly derived from trimethylbrazilin, and a number of further experiments which we have made with this substance and its derivatives seem to us to indicate clearly that it is formed according to the following scheme.

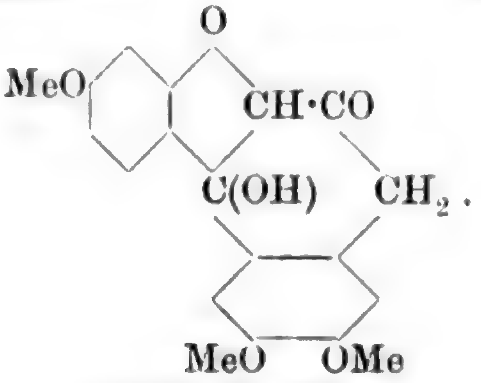
The oxidation of trimethylbrazilin with chromic acid leads to the disruption of the central linking, and the unstable diketone which is thus formed undergoes aldol condensation and yields trimethylbrazilone:



Trimethylbrazilin.



Diketone.



Trimethylbrazilone.

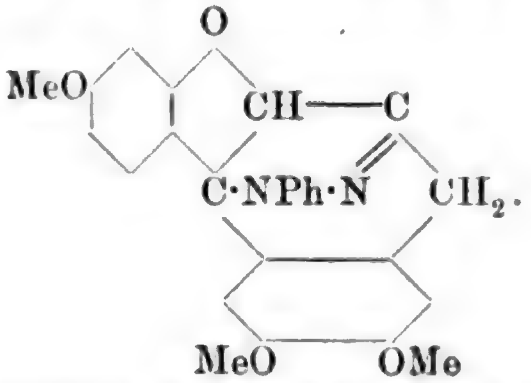
This formula represents trimethylbrazilone as a derivative both of coumaran and of tetrahydronaphthalene, and affords a ready explanation of all the decompositions of this substance.

That trimethylbrazilone is a ketone is proved by the preparation of an oxime (Herzig and Pollak, *Ber.*, 1903, **36**, 398), and by the fact that it reacts readily with phenylhydrazine, but in the latter case the process leads, under different conditions, to widely different products.

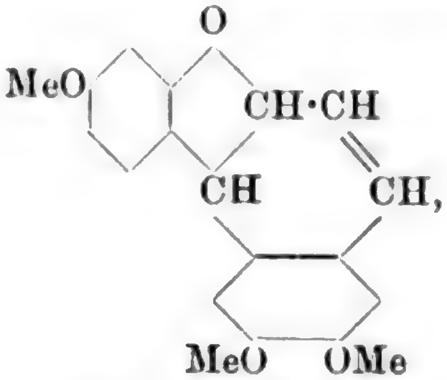
Herzig and Pollak (*Ber.*, 1905, **38**, 2166) heated trimethylbrazilone with acetic acid and phenylhydrazine on the water-bath, and obtained a substance, $C_{22}H_{13}ON_2(OMe)_3$, which crystallised in yellow needles and melted at 239—242°. This phenylhydrazine derivative is produced according to the equation:

$$C_{16}H_9O_3(MeO)_3 + C_6H_5\cdot NH\cdot NH_2 = C_{22}H_{13}ON_2(OMe)_3 + 2H_2O,$$

and it is obviously a pyrazoline derivative. The formation of such a substance is readily understood with the aid of the above formula for trimethylbrazilone, and its constitution is doubtless

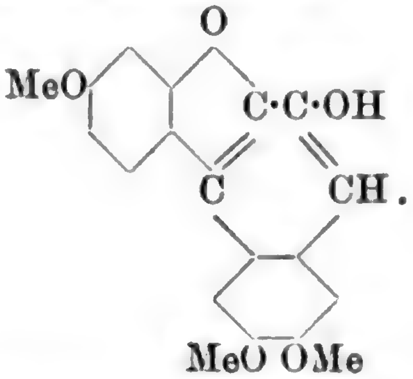


When trimethylbrazilone is boiled in glacial acetic acid solution with phenylhydrazine, an entirely different reaction takes place, and leads to the formation of a substance, $C_{16}H_{10}O_3(MeO)_3$, which is described in an earlier paper (Trans., 1902, **81**, 1040) under the name deoxytrimethylbrazilone. This substance is probably a dihydronaphthalene derivative of the formula



but the position of the additive hydrogen atoms is uncertain.

The most important evidence in favour of the correctness of the above view of the constitution of trimethylbrazilone is obtained from the study of the properties of *a-anhydrotrimethylbrazilone*. This substance is produced by the action of alkalis, acetic anhydride, or some other dehydrating agents on trimethylbrazilone, and there can be little doubt that its formation is due simply to the elimination of water from the aldol grouping in trimethylbrazilone, and that it therefore has the constitution:



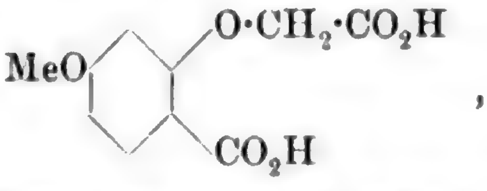
This formula represents *α*-anhydrotrimethylbrazilone as a derivative of *β*-naphthol, and, in accordance with this view, we find that it shows many of the properties of *β*-naphthol. It dissolves in cold dilute potash, and the alkaline solution combines readily with diazobenzene chloride to yield an intense red azo-dye, which is almost exactly similar to the dye which is produced from *β*-naphthol under the same conditions. In particular, it shows the characteristic property of dissolving in concentrated sulphuric acid with an intense red colour. Again, when *α*-anhydrotrimethylbrazilone is combined with *α*-diazonaphthalene chloride, the azo-dye produced dissolves in concentrated sulphuric acid with a blue colour exactly as in the case of the dye produced from *β*-naphthol.

The most striking reaction of trimethylbrazilone is its behaviour with cold concentrated nitric acid, when it yields nitrohydroxydihydrotrimethylbrazilone (Trans., 1902, **81**, 1049):

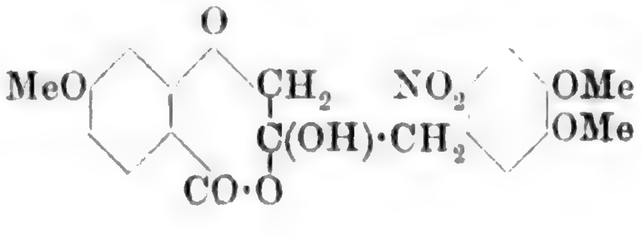
$$C_{16}H_9O_3(MeO)_3 + HNO_3 = C_{16}H_{10}O_6N(MeO)_3.$$

This remarkable substance dissolves in alkalis with an intense purple colour, but, on standing, the colour rapidly fades, *o*-nitrohomocatechol separates, and the solution contains *p*-methoxysalicylic acid.

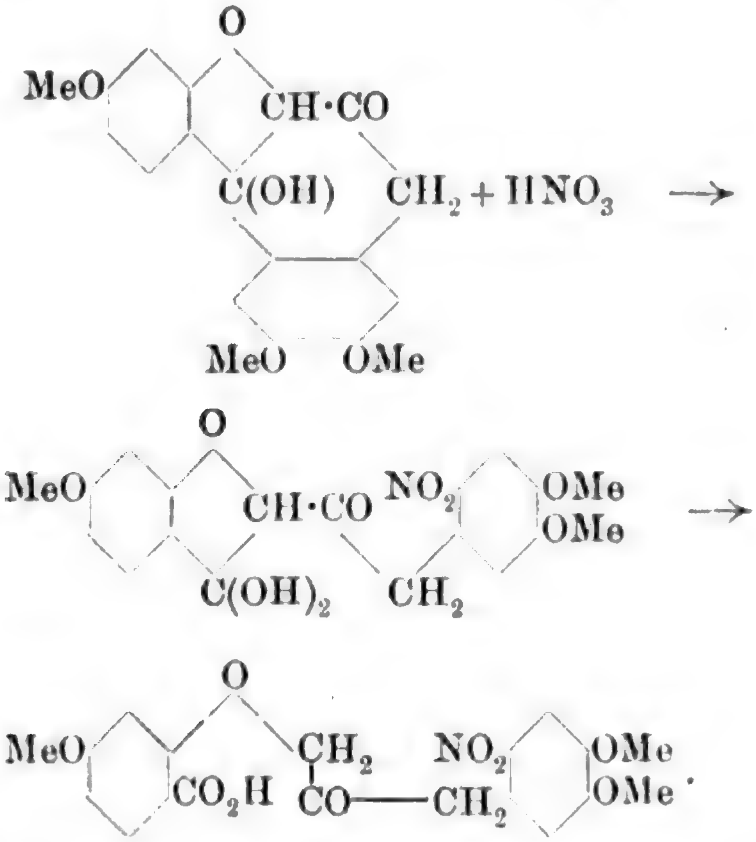
When oxidised with permanganate, nitrohydroxydihydrotrimethylbrazilone yields 2-carboxy-5-methoxyphenoxyacetic acid,



and these decompositions point clearly to the formula

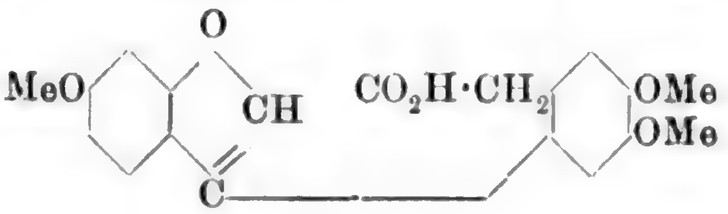


as the constitution of the nitro-compound (compare Trans., 1902, **81**, 1059). This expression is derived from the constitutional formula for trimethylbrazilone in the following manner:

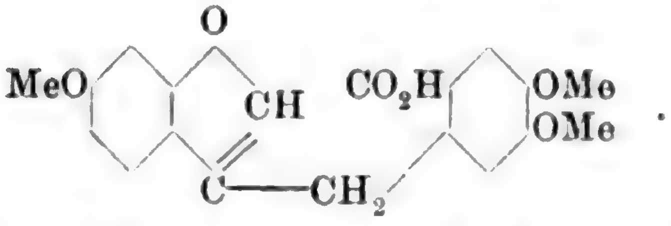


The substance last represented undergoes a simple intramolecular change, and the lactone, nitrohydroxydihydrotrimethylbrazilone, is produced.

Herzig (*Ber.*, 1904, **37**, 631) has shown that trimethylbrazilone undergoes isomeric change when it is dissolved in sulphuric acid, and yields ψ-trimethylbrazilone. This substance is a monobasic acid, and, in the course of its investigation, we found that, on oxidation with permanganate, it yields large quantities of 2-carboxy-4 : 5-dimethoxyphenylacetic acid, $(MeO)_2C_6H_2(CO_2H)\cdot CH_2\cdot CO_2H$ (compare p. 516). There can be little doubt therefore that its constitution is represented by one of the formulæ:

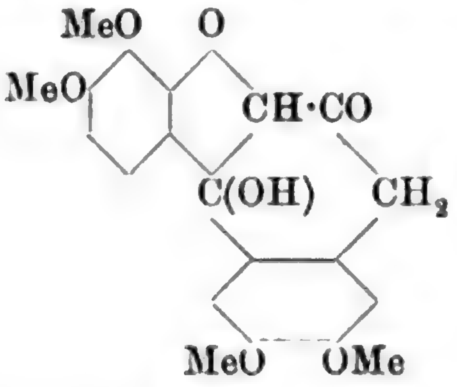


or

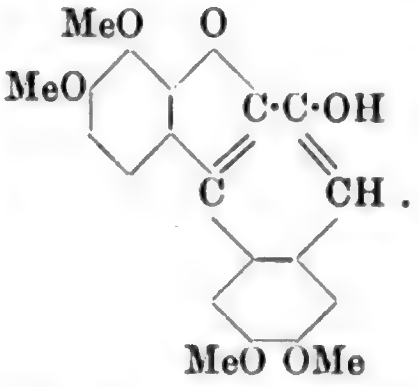


and its formation from trimethylbrazilone may be readily followed with the aid of the formula suggested above.

When tetramethylhæmatoxylin is oxidised with chromic acid, it behaves in an exactly similar manner to trimethylbrazilin, and yields tetramethylhæmatoxylone (Trans., 1902, **81**, 1060), and the latter substance is converted by alkalis or dehydrating agents into anhydrotetramethylhæmatoxylone. The constitutions of these substances may therefore be represented thus:



and



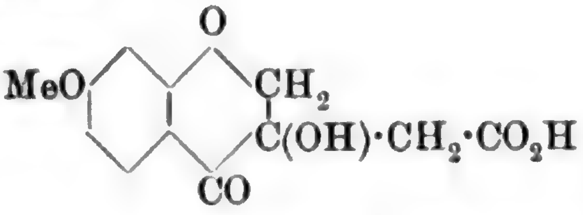
In support of these formulæ, the fact may be specially mentioned that anhydrotetramethylhæmatoxylone, like anhydrotrimethylbrazilone, exhibits all the properties of a derivative of β-naphthol.

We are at present engaged on a series of experiments with the object of synthesising trimethylbrazilone, tetramethylhæmatoxylone, and their derivatives, and, in this way, of definitely establishing their constitutions.

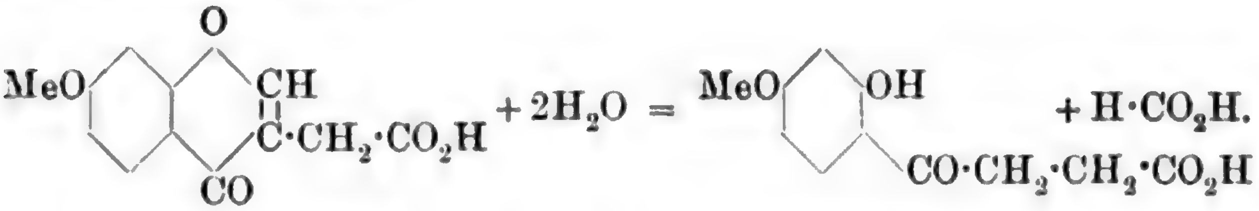
Constitution of Brazilic Acid and Synthesis of Anhydrobrazilic Acid.

It has already been pointed out in this introduction (p. 491) that the determination of the constitution of brazilic acid is of the greatest importance, not only on account of the interest attaching to the acid itself, but more particularly because the constitution of brazilic acid has such a direct bearing on that of brazilin.

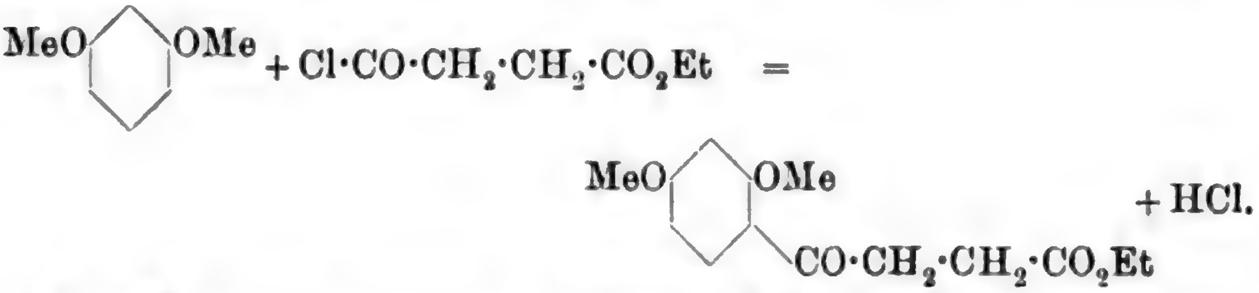
This matter has been fully discussed in an earlier paper (Trans., 1902, **81**, 221), and it is there shown that all the available evidence pointed to the formula



as correctly representing brazilic acid. The most important decomposition of this acid is its conversion into anhydrobrazilic acid by concentrated sulphuric acid, a change which is simply due to elimination of water. Evidence of the constitution of the anhydro-acid is afforded by its decomposition by baryta into formic acid and 2-hydroxy-4-methoxybenzoylpropionic acid, a change which may be represented thus:

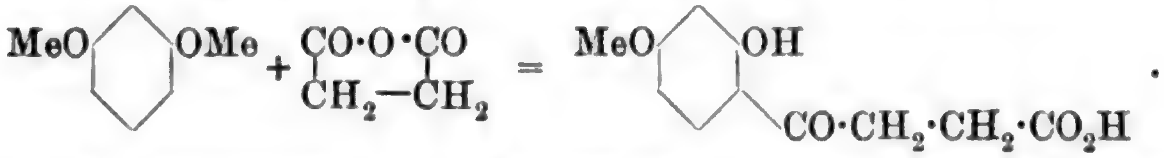


In order to control this view of the decomposition, the hydroxymethoxybenzoylpropionic acid was methylated and the dimethoxy-derivative prepared synthetically from resorcinol dimethyl ether, the ester of the semi-chloride of succinic acid and aluminium chloride:

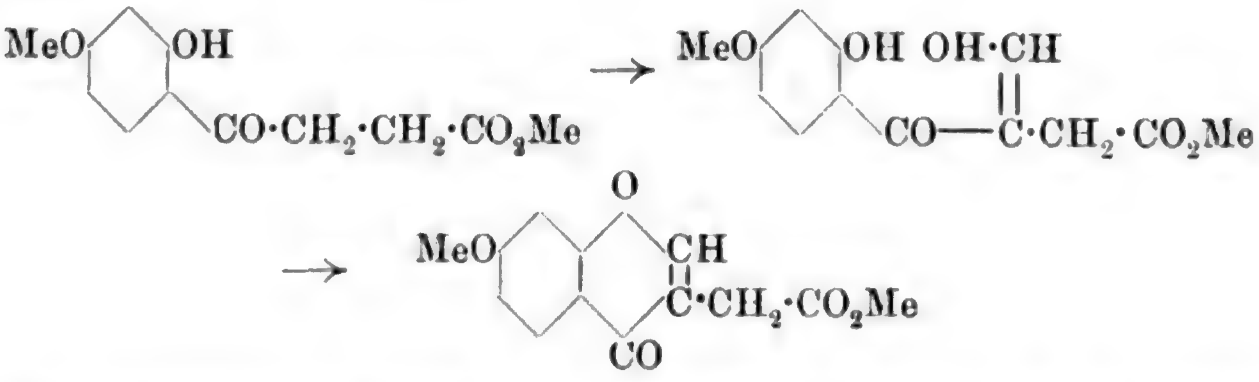


A still more convenient synthesis of this acid has since been devised, and is described on p. 506.

Although all this evidence is very strongly in favour of the above constitution of anhydrobrazilic acid, we wished to be quite certain on this point, and therefore decided to attempt the synthesis of this acid, a problem which proved to be much more difficult than we, at first, anticipated. Such of the unsuccessful attempts as have led to the preparation of new compounds of interest are described in the experimental part of this paper (pp. 505, 507), and the synthesis of anhydrobrazilic acid was ultimately accomplished in the following manner. The starting point is 2-hydroxy-4-methoxybenzoylpropionic acid, which is produced when a mixture of resorcinol dimethyl ether and succinic anhydride is treated with aluminium chloride without employing a solvent. Under these conditions, a vigorous reaction sets in, and condensation and elimination of a methyl group take place at the same time,



and it is interesting that the substance thus produced is identical with the acid which is obtained when anhydrobrazilic acid is digested with baryta water (see above). When the methyl ester of hydroxymethoxybenzoylpropionic acid is dissolved in ethyl formate and treated with finely divided sodium, a vigorous reaction sets in, and the product contains the methyl ester of anhydrobrazilic acid, since it yields this acid on hydrolysis. This interesting synthesis of anhydrobrazilic acid may be represented in the following way:

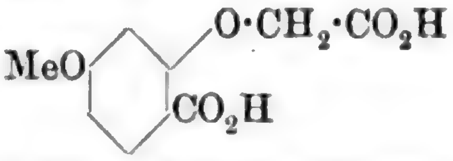


and conclusively proves not only the constitution of anhydrobrazilic acid, but also indirectly that of brazilic acid itself.

EXPERIMENTAL.

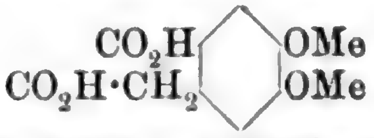
Synthesis of 2-Carboxy-5-methoxyphenoxyacetic Acid.

It has already been pointed out (pp. 490, 492) that the two acids:



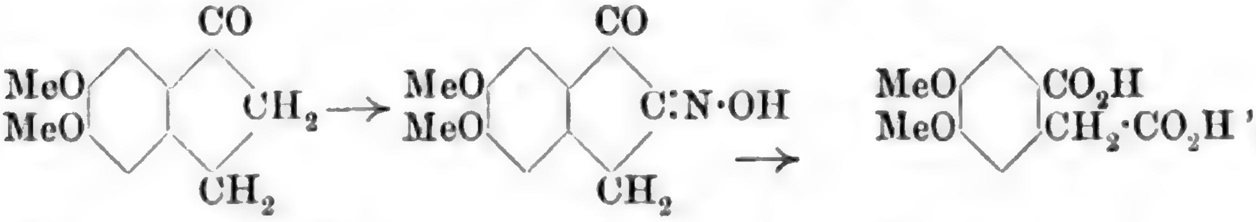
2-Carboxy-5-methoxyphenoxyacetic acid.

and



2-Carboxy-4 : 5-dimethoxyphenylacetic acid.

are amongst the most important degradation products of trimethylbrazilin. The synthesis of the last mentioned of these acids from 5 : 6-dimethoxy-1-hydrindone by the following steps:



has been described in an earlier paper (Trans., 1907, **91**, 1082). We have now succeeded in synthesising 2-carboxy-5-methoxyphenoxyacetic acid, and there can therefore be no doubt as to the constitution of either of these acids. The first step in the synthesis was the preparation of aldehydomethoxyphenoxyacetic acid, $MeO \cdot C_6H_3(O \cdot CH_2 \cdot CO_2H) \cdot CHO$, and this was accomplished in the following way.

p-Methoxysalicylaldehyde (3 grams) was mixed with chloroacetic acid (5 grams), and sufficient hot 40 per cent. potassium hydroxide slowly added to keep the clear yellow liquid distinctly alkaline; the product was then boiled for half an hour. The solution of the potassium salt of aldehydo-*p*-methoxyphenoxyacetic acid thus obtained was diluted with water, cooled, and potassium permanganate added until the pink colour remained permanent. The whole was then heated to boiling, filtered, and the filtrate and washings of the manganese precipitate concentrated and, while still hot, acidified with hydrochloric acid, when colourless needles separated, which, after recrystallisation from water, gave the following results on analysis:

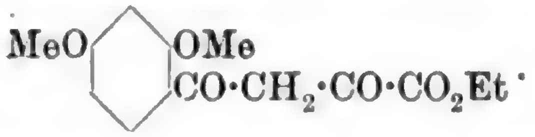
0·1466 gave 0·2846 CO_2 and 0·0584 H_2O. C=52·9; H=4·4.

$C_{10}H_{10}O_6$ requires C=53·1; H=4·4 per cent.

2-*Carboxy*-5-*methoxyphenoxyacetic acid* melts at 175°, and is identical with the acid obtained by the oxidation of trimethylbrazilin (Trans., 1901, **79**, 1407), and which was assumed to have this constitution.

The identity was proved not only by the comparison of the general properties of the two specimens, but also by the fact that, when mixed, the mixture melted at the same point (175°) as the constituents.

Ethyl 2:4-*Dimethoxybenzoylpyruvate*,



This substance was prepared because it was thought that it might prove valuable in our experiments on the synthesis of anhydrobrazilic acid, and the process employed was similar to that described by Kostanecki, Paul, and Tambor (*Ber.*, 1901, **34**, 2477) in their experiments with the corresponding diethoxy-derivative. A mixture of resacetophenone dimethyl ether (3 grams) and ethyl oxalate (7 grams) was added to finely-divided sodium* (0·7 gram), when a vigorous action soon set in, and the sodium rapidly and completely disappeared. Owing to the separation of a yellow sodium salt, the product of the reaction was nearly solid. After decomposing with dilute acetic acid, the yellow, crystalline precipitate was collected, well washed, and crystallised from alcohol:

0·1209 gave 0·2652 CO_2 and 0·0627 H_2O. C=59·8; H=5·8.

$C_{14}H_{16}O_6$ requires C=60·0; H=5·7 per cent.

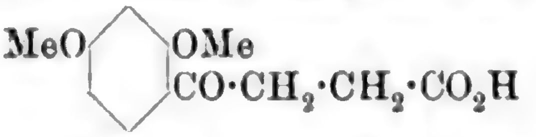
Ethyl 2:4-*dimethoxybenzoylpyruvate* crystallises in beautiful golden-yellow flakes, melts at 86—87°, and its solution in alcohol gives, on the addition of ferric chloride, a brownish-green coloration. When the dry substance is heated in a test-tube, it decomposes with evolution of carbon monoxide and formation of an oil which yields a violet coloration when ferric chloride is added to its alcoholic solution. This oil is soluble in alkaline carbonates, and obviously consists of ethyl 2:4-dimethoxybenzoylacetate, $(MeO)_2C_6H_3\cdot CO\cdot CH_2\cdot CO_2Et$. Ethyl dimethoxybenzoylpyruvate is readily hydrolysed by alkalis with formation of dimethoxybenzoylpyruvic acid.

---

* The finely-divided sodium used in all our experiments was prepared by melting sodium under toluene and agitating vigorously.

This acid is not readily decomposed by the further action of alkalis, but, when boiled with strong potash, the yellow colour of the solution gradually becomes fainter, and dimethoxyacetophenone may then be extracted with ether. Many attempts were made to cause the sodium derivative of ethyl dimethoxybenzoylpyruvate to react with chloro- or bromo-acetic ester, but without success, and this is perhaps hardly surprising in view of the fact that oxalacetic ester yields alkyl derivatives only with great difficulty.

2:4-*Dimethoxybenzoylpropionic Acid*,



The synthesis of this acid from resorcinol dimethyl ether and the ester of the semi-chloride of succinic acid and subsequent hydrolysis has been described in an earlier paper (Trans., 1902, **81**, 234), but the yield obtained was very unsatisfactory. We have now found that this acid may be readily prepared from resorcinol dimethyl ether by condensation with succinic anhydride in the presence of aluminium chloride. Resorcinol dimethyl ether (30 grams) is dissolved in carbon disulphide (200 grams), and succinic anhydride (20 grams) and aluminium chloride (25 grams) added alternately in small quantities at a time, when a vigorous action sets in, but subsides in about fifteen minutes.

The whole is heated in a reflux apparatus on the water-bath for three hours, the dark red, syrupy aluminium compound is decomposed by ice, and the product distilled in steam to remove carbon disulphide. The residue in the distillation flask solidifies on cooling, and, after several crystallisations from benzene, melts at 146—148°, and consists of pure *dimethoxybenzoylpropionic acid*:

0·1607 gave 0·3560 CO_2 and 0·0873 H_2O. C = 60·4; H = 6·0.

$C_{12}H_{14}O_5$ requires C = 60·5; H = 5·9 per cent.

The acid thus obtained became a deep violet a few degrees above its melting point, a reaction which is characteristic of dimethoxybenzoylpropionic acid. That the synthetical acid is identical with the acid obtained from anhydrobrazilic acid (*loc. cit.*, p. 233) was proved by the fact that, when the two specimens were mixed, there was no alteration in the melting point.

Methyl 2:4-Dimethoxybenzoylpropionate, $(MeO)_2C_6H_3\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2Me$.

This substance is readily obtained by boiling the acid (5 grams) with methyl alcohol (50 c.c.) and sulphuric acid (5 c.c.) in a reflux apparatus for two hours. The product is poured into water, extracted with ether, the ethereal solution washed with dilute sodium carbonate, dried over calcium chloride, and the ether evaporated, when an oil is obtained which soon solidifies, especially if a crystal is introduced. After leaving in contact with porous porcelain until the oily impurities had been completely absorbed, the residue was recrystallised from light petroleum:

0·1734 gave 0·3921 CO_2 and 0·0965 H_2O. C=61·7; H=6·2.
$C_{13}H_{16}O_5$ requires C=61·9; H=6·3 per cent.

Methyl dimethoxybenzoylpropionate separates from light petroleum in small, colourless prisms, and melts at 58°.

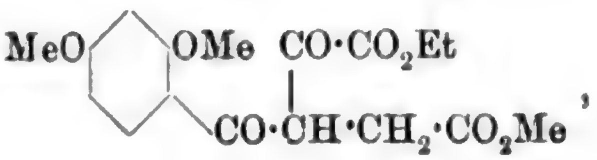
Condensation of Methyl 2:4-Dimethoxybenzoylpropionate with Ethyl Oxalate.

In studying this condensation, the methyl ester (5 grams) was dissolved in ethyl oxalate (15 grams), and then finely-divided sodium (1·5 grams) added gradually. The addition of each quantity of sodium produced a vigorous reaction, which was regulated by cooling under the tap.

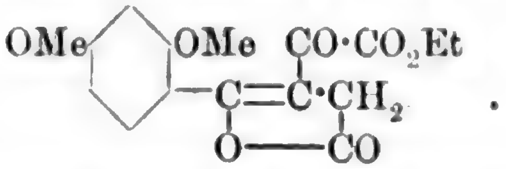
When the whole of the sodium had been added, the brownish-yellow mass was heated for ten minutes on the water-bath, and decomposed by dilute acetic acid. The yellow precipitate was collected at the pump and recrystallised from alcohol, in which it is sparingly soluble, and from which it separates in brownish-yellow needles or prisms, which melt at 170°. Two different preparations gave the following results on analysis:

0·1916 gave 0·4203 CO_2 and 0·0828 H_2O. C=59·8; H=4·8.
0·1320 „ 0·2897 CO_2 „ 0·0600 H_2O. C=59·9; H=5·0.
$C_{16}H_{16}O_7$ requires C=60·0; H=5·0 per cent.

The product which should result from methyl dimethoxybenzoylpropionate by condensation with ethyl oxalate should have the constitution:

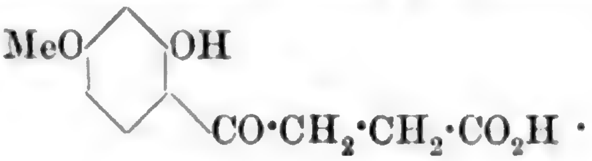


and, as the substance actually obtained contained methyl alcohol less than this, it is evidently a lactone of the probable constitution:



This lactone gives, in alcoholic solution, a brown coloration with ferric chloride, when heated it decomposes with evolution of carbon monoxide, and, when digested with alkalis, it is hydrolysed with formation of dimethoxybenzoylpropionic acid. It seemed probable that this lactone would be of value in our experiments on the synthesis of anhydrobrazilic acid, but, as this did not prove to be the case, it was not further investigated.

2-Hydroxy-4-methoxybenzoylpropionic Acid,



It has already been pointed out that aluminium chloride reacts with a mixture of succinic anhydride and resorcinol dimethyl ether in the presence of carbon disulphide with the formation of dimethoxybenzoylpropionic acid, $(MeO)_2C_6H_3\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2H$. When, however, the condensation is carried out in the absence of the solvent, hydrolysis of the methoxy-group adjacent to the carbonyl group takes place at the same time, and hydroxymethoxybenzoylpropionic acid is formed. Resorcinol dimethyl ether (15 grams) and succinic anhydride (10 grams) are melted together, and aluminium chloride (10 grams) added, when a vigorous action sets in, and, after this has slackened, a further quantity of aluminium chloride (10 grams) is added and the mixture heated on the water-bath for three hours. The bright red, rather stable aluminium compound is decomposed by warm dilute hydrochloric acid, the brown oil which separates extracted with ether, the ethereal solution filtered and extracted with sodium carbonate. The alkaline extract is boiled with purified animal charcoal, filtered, and acidified while still hot, when brown needles separate, which, after several crystallisations from water, are obtained quite colourless:

0·1310 gave 0·2815 CO_2 and 0·0630 H_2O. C = 58·6; H = 5·3.

$C_{11}H_{12}O_5$ requires C = 58·9; H = 5·3 per cent.

The *2-hydroxy-4-methoxybenzoylpropionic acid*, obtained in this way, melted at 156°, and was identical with the acid of this composition which had previously been obtained (Trans., 1902, **81**,

231) from anhydrobrazilic acid by treatment with baryta, since no alteration in melting point could be detected when the two specimens were mixed.

Methyl Hydroxymethoxybenzoylpropionate, $(MeO)(OH)C_6H_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Me$.

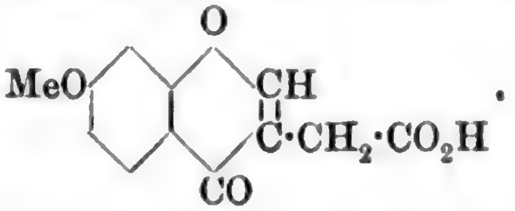
This ester is readily obtained when the acid is boiled for two hours with twenty times its weight of methyl alcohol, containing 20 per cent. of sulphuric acid. The product is poured into water, rendered alkaline by sodium carbonate, and the solid ester collected at the pump, washed, and recrystallised from dilute methyl alcohol:

0·1264 gave 0·2787 CO_2 and 0·0684 H_2O. C = 60·1; H = 6·0.

$C_{12}H_{14}O_5$ requires C = 60·5; H = 5·9 per cent.

Methyl hydroxymethoxybenzoylpropionate separates from dilute methyl alcohol in colourless needles, melts at 87°, and gives an intense violet coloration when ferric chloride is added to its alcoholic solution.

Synthesis of Anhydrobrazilic Acid,



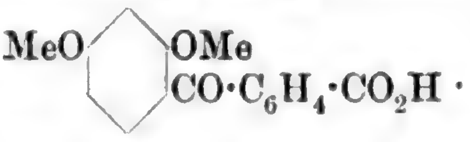
This synthesis, which has been discussed in the introduction (p. 504), was carried out in the following way. Methyl hydroxymethoxybenzoylpropionate (3 grams) was dissolved in hot ethyl formate (10 grams), and then finely-divided sodium (1 gram) added, when a reaction set in which was allowed to proceed vigorously and yet kept under control by cooling from time to time somewhat with water. The yellow product was freed from traces of sodium by mixing with a little alcohol, and then warmed on the water-bath with concentrated hydrochloric acid for fifteen minutes. After extracting with ether, the ethereal solution was evaporated, and the residual oil hydrolysed by boiling with excess of methyl-alcoholic potash; the solution was then diluted, evaporated on the water-bath until free from methyl alcohol, acidified with hydrochloric acid, digested with animal charcoal, and filtered hot. The filtrate deposited on standing a yellow, crystalline powder, which was recrystallised several times from water, and until it no longer gave a violet coloration with ferric chloride:

0·1298 gave 0·2914 CO_2 and 0·0505 H_2O. C = 61·2; H = 4·3.

$C_{12}H_{10}O_5$ requires C = 61·5; H = 4·3 per cent.

That this substance is *anhydrobrazilic acid* (Trans., 1902, **81**, 230) was proved by the fact that it showed the following characteristic properties of that acid. It melted at 197°, gave no coloration with ferric chloride, and, when dissolved in concentrated sulphuric acid, it yielded a colourless solution, which fluoresced faintly blue in diffused light, and very brilliantly so in the light of burning magnesium. Moreover, a mixture of the synthetical acid and the acid obtained from trimethylbrazilin melted at exactly the same temperature as the components.

2′:4′-Dimethoxybenzoylbenzoic Acid,



Our experiments on the synthesis of brazilinic acid and the lactones of dihydrobrazilinic and dihydrohæmatoxylinic acids, necessitated the condensation of various substances with *m*-hemipinic anhydride, and, as this substance is very difficult to prepare in quantity, we, in all cases, first worked out the conditions of condensation with phthalic anhydride in the place of *m*-hemipinic anhydride.

These experiments are described in the following sections.

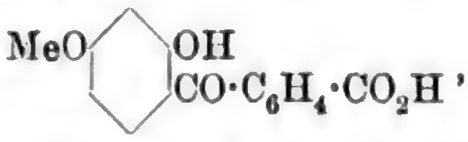
2′:4′-Dimethoxybenzoylbenzoic acid was prepared under the following conditions. Phthalic anhydride (15 grams) and resorcinol dimethyl ether (20 grams) were mixed with carbon disulphide (100 grams) and aluminium chloride (20 grams), and boiled on the water-bath for four hours, when a dark red aluminium compound separated. After this had been carefully decomposed by ice, the whole was distilled in steam to remove the carbon disulphide and unchanged resorcinol dimethyl ether, and then cooled, when the oily product soon solidified, and the solution also became filled with crystals of the new acid.

The solid was collected and crystallised from dilute acetic acid:

0·1274 gave 0·3129 CO_2 and 0·0587 H_2O. C=67·0; H=5·1.

$C_{16}H_{14}O_5$ requires C=67·1; H=4·9 per cent.

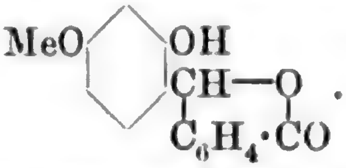
2′:4′-*Dimethoxybenzoylbenzoic acid* separates from dilute acetic acid in colourless prisms, and melts at 164°. When heated in small quantities with fuming hydriodic acid, it yields 2′-hydroxy-4′-methoxybenzoylbenzoic acid,



the methoxy-group adjacent to the carbonyl group suffering hydrolysis. The acid thus obtained gave a purple coloration when ferric chloride was added to its alcoholic solution.

It had already been prepared by Quenda (*Gazzetta*, 1890, **20**, 128) from phthalic anhydride and resorcinol dimethyl ether by heating on the water-bath with aluminium chloride without using a diluent.

2-*Hydroxy-4-methoxyphenylphthalide*,



This substance is readily obtained by the reduction of 2′-hydroxy-4′-methoxybenzoylbenzoic acid with sodium amalgam. The acid is dissolved in dilute sodium carbonate and treated, in a porcelain beaker fitted with a mechanical stirrer, with an excess of 2·5 per cent. sodium amalgam prepared from freshly-distilled mercury.

After remaining overnight, the solution is diluted, and sufficient dilute hydrochloric acid added to precipitate the impurities.

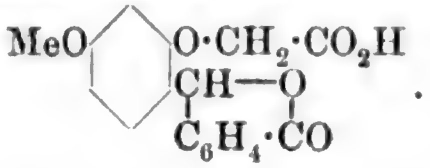
The liquid is then decanted from the tarry matter and acidified with excess of hydrochloric acid, when the lactone separates in almost colourless crystals, and may be recrystallised by dissolving in hot ethyl acetate and adding a few drops of light petroleum (b. p. 35—50°):

0·1513 gave 0·3886 CO_2 and 0·0630 H_2O. C = 70·1; H = 4·6.

$C_{15}H_{12}O_4$ requires C = 70·3; H = 4·7 per cent.

2-*Hydroxy-4-methoxyphenylphthalide* crystallises in colourless prisms, and melts at 175°. It dissolves in concentrated sulphuric acid with a yellow colour, which does not fade even after several hours.

2-*Phthalide-5-methoxyphenoxyacetic Acid*,



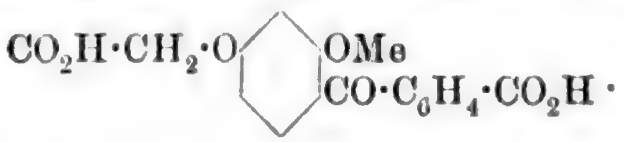
This interesting substance is closely related to the lactones of dihydrobrazilinic and dihydrohæmatoxylinic acids, and is obtained from 2-hydroxy-4-methoxyphenylphthalide by the action of chloroacetic acid and potassium hydroxide under the following conditions.

The phthalide (2 grams) is mixed with chloroacetic acid (10 grams) and water (10 c.c.), heated to boiling, and then potassium hydroxide (40 per cent.) added from time to time, so that the solution is always distinctly alkaline. A vigorous action takes place, and is complete in about a quarter of an hour. The product is diluted with water, acidified, and the colourless precipitate collected and crystallised from acetic ester and a little light petroleum:

0·0771 gave 0·1840 CO_2 and 0·0308 H_2O. C = 65·1; H = 4·4.
$C_{17}H_{14}O_6$ requires C = 65·0; H = 4·4 per cent.

2-Phthalide-5-methoxyphenoxyacetic acid melts at 188°, dissolves readily in sodium carbonate, and the solution does not decolorise permanganate. It dissolves in concentrated sulphuric acid, yielding a yellow solution which, on standing, rapidly fades and soon becomes almost colourless, and in this it closely resembles the behaviour of the lactones of dihydrobrazilinic and dihydrohæmatoxylinic acids under the same conditions.

4-Phthaloyl-3-methoxyphenoxyacetic Acid,

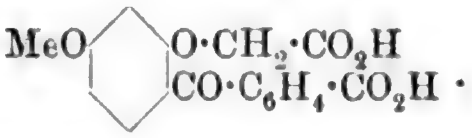


In preparing this substance, 3-methoxyphenoxyacetic ester (50 grams) and phthalic anhydride (40 grams) are mixed with carbon disulphide (100 grams) and aluminium chloride (50 grams), and boiled on the water-bath for four hours. The red aluminium compound is decomposed by ice and dilute hydrochloric acid, and the carbon disulphide removed by distillation in steam; the brown oil remaining in the flask is dissolved in strong potash, and boiled in order to hydrolyse any ester which might be present. The hot liquid is acidified, decanted from the dark oil, and cooled, when a yellow oil is obtained, which is boiled with three litres of water, and the clear liquid filtered and allowed to cool. The nearly colourless oil which is deposited is dissolved in acetic acid and carefully precipitated with water, when, on long standing, colourless crystals separate in small quantity. These are collected, drained on porous porcelain, and recrystallised from dilute acetic acid:

0·1061 gave 0·2386 CO_2 and 0·0418 H_2O. C = 61·3; H = 4·4.
$C_{17}H_{14}O_7$ requires C = 61·8; H = 4·2 per cent.

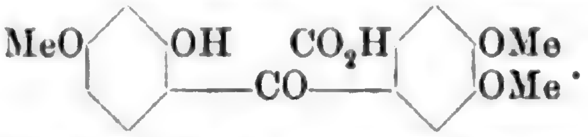
4-Phthaloyl-3-methoxyphenoxyacetic acid crystallises in small, colourless prisms, melts at 144—146°, and dissolves in sulphuric acid, yielding an intense orange solution which does not fade on standing.

The above condensation product of methoxyphenoxyacetic ester and phthalic anhydride might conceivably have had the constitution:



and have yielded 2-phthalide-5-methoxyphenoxyacetic acid (m. p. 188°, p. 511) on reduction. Since, however, the product actually obtained by reduction with sodium amalgam was found to melt at 156°, there can be little doubt that the phthaloyl compound has the constitution assigned to it at the head of this section.

2′-*Hydroxy*-4′ : 4 : 5-*trimethoxy*-2-*benzoylbenzoic Acid*,



A satisfactory yield of this condensation product is obtained under the following conditions. *m*-Hemipinic anhydride (3 grams) is mixed with resorcinol dimethyl ether (4 grams) in a large test-tube, the mixture is then heated to 150°, and aluminium chloride (6 grams) added all at once. A vigorous action sets in, and a violet aluminium compound separates, and, after remaining until cold, the compound is decomposed by heating with water on the water-bath.

The product is extracted several times with ether, the ethereal solution well agitated with sodium carbonate, the aqueous layer is then separated, boiled until free from ether, cooled, and acidified.

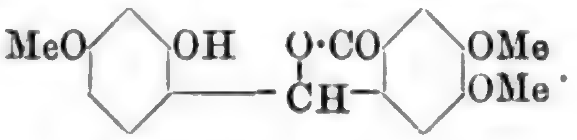
After collecting at the pump, the chalky yellow precipitate is purified by boiling with much water, filtering, and allowing to cool, and the pale yellow powder is then dried over sulphuric acid in an evacuated desiccator:

0·1180 gave 0·2641 CO_2 and 0·0513 H_2O. C = 61·0; H = 4·8.

$C_{17}H_{16}O_7$ requires C = 61·4; H = 4·8 per cent.

This substance could not be obtained in a definite crystalline condition, and it has no definite melting point. It yields an intense red solution with sulphuric acid, and the shade of colour is precisely the same as that produced by brazilinic acid under the same conditions; in both cases, the colour disappears on the addition of water.

2-m-*Meconyl*-5-*methoxyphenol*,



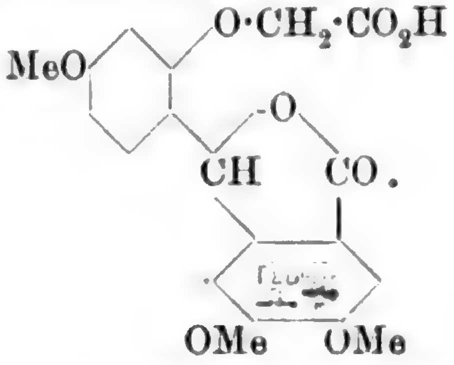
This substance is obtained when hydroxytrimethoxybenzoylbenzoic acid (see the last section) is treated with excess of freshly-prepared sodium amalgam for twelve hours, care being taken, by the frequent addition of small quantities of dilute hydrochloric acid, that the liquid is always only slightly alkaline. The product is acidified, and the crystalline precipitate collected, washed well, and crystallised from ethyl acetate:

0·1352 gave 0·3186 CO_2 and 0·0622 H_2O. C = 64·3; H = 5·1.

$C_{17}H_{16}O_6$ requires C = 64·5; H = 5·0 per cent.

2-m-*Meconyl-5-methoxyphenol* melts at 206—207°, and dissolves in sulphuric acid, yielding an orange-red solution, the colour of which does not diminish in intensity on standing. But for this latter fact, the reaction is identical with that shown by the lactone of dihydrobrazilinic acid (Trans., 1902, **81**, 1039).

Synthesis of the Lactone of Dihydrobrazilinic Acid,



In carrying out this synthesis, 2-*m*-meconyl-5-methoxyphenol was mixed with a little water and an excess of chloroacetic acid, and enough concentrated aqueous potassium hydroxide was added to make a clear solution.

The whole was then boiled for half an hour, small quantities of concentrated aqueous potassium hydroxide being added from time to time, so that the liquid was always distinctly alkaline. When the product was cooled and acidified, a chalky powder separated, which was collected, washed well, and crystallised several times from dilute acetic acid:

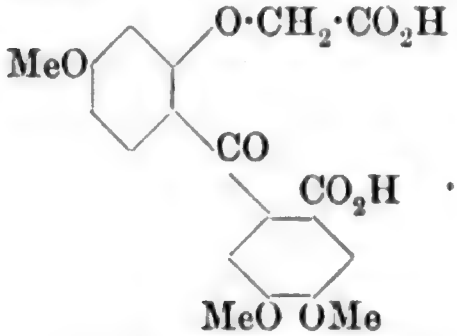
0·1219 gave 0·2724 CO_2 and 0·0540 H_2O. C = 60·9; H = 4·9.

$C_{19}H_{18}O_8$ requires C = 61·0; H = 4·8 per cent.

That this substance is identical with the *lactone* of *dihydrobrazilinic acid*, which is produced when brazilinic acid is reduced with sodium amalgam (Trans., 1902, **81**, 1038), is proved by the above analysis and the following properties of the synthetical substance.

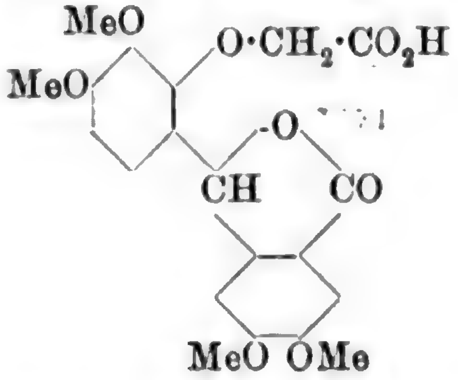
It melts at 227°, crystallises in minute balls of needles, and dissolves in sulphuric acid with a deep red colour, which rapidly fades and becomes pale yellow. Moreover, a mixture of equal quantities of the synthetical lactone and the lactone from brazilinic acid melts at the same temperature as the components.

Synthesis of Brazilinic Acid,



When a mixture of *m*-hemipinic anhydride (3 grams) and ethyl 3-methoxyphenoxyacetate is diluted with carbon disulphide and digested on the water-bath with aluminium chloride (10 grams) for half an hour, a red aluminium compound is produced. The carbon disulphide is decanted, the compound is decomposed by water (50 c.c.), and concentrated aqueous potassium hydroxide added until solution is complete. After warming on the water-bath for a few minutes, boiling water (500 c.c.) is added, the alkaline solution acidified, and allowed to remain in a cool place for some days. The small quantity of precipitate which will have separated is collected and crystallised several times from dilute acetic acid, when a colourless, crystalline substance is obtained, which melts at 208—209° and consists of *brazilinic acid*, since when mixed with brazilinic acid obtained by the oxidation of trimethylbrazilin (Trans., 1902, **81**, 1030) no alteration in melting point could be detected. The synthetical acid also dissolved in sulphuric acid with the red colour so characteristic of brazilinic acid.

Synthesis of the Lactone of Dihydrohaematoxylinic Acid,



This interesting synthesis was accomplished under the following conditions. *m*-Hemipinic anhydride (3 grams) and pyrogallol trimethyl ether (4 grams) were melted together and allowed to cool until the temperature was 150°. Aluminium chloride (8 grams) was then added, when a vigorous reaction ensued, and, as soon as this had moderated, the deep red aluminium compound which had separated was decomposed by water and the product extracted several times with ether.

The ethereal solution was extracted with sodium carbonate, and the alkaline extract left in contact with an excess of freshly-prepared sodium amalgam for four hours and then acidified. The brown precipitate was collected, dissolved in potash solution, and boiled with an excess of chloroacetic acid for ten minutes, care being taken that the liquid always remained alkaline. After acidifying, the gelatinous precipitate was collected, washed well, and crystallised from dilute acetic acid with the aid of animal charcoal, when the pure substance separated as a voluminous mass of slender needles. Careful comparison showed that this substance was the *lactone* of *dihydrohaematoxylinic acid.* It melted at 192°, and the same melting point was observed when it was mixed with a specimen of the lactone which had been prepared from hæmatoxylin (Trans., 1902, **81**, 244). Furthermore, the synthetical lactone dissolved in sulphuric acid with a red colour, which became salmon-pink on standing, and, on warming, the colour changed to red, then to violet, and finally to brown.

This reaction is characteristic of the lactone of dihydrohæmatoxylinic acid.

Oxidation of ψ-Trimethylbrazilone to 2-Carboxy-4:5-dimethoxyphenylacetic Acid.

It has been pointed out that ψ-trimethylbrazilone is produced when trimethylbrazilone is dissolved in concentrated sulphuric acid (Herzig, *Ber.*, 1904, **37**, 631), and, in order to obtain some evidence of its constitution, its behaviour on oxidation with permanganate was investigated. Pure ψ-trimethylbrazilone (as obtained after repeated recrystallisation from ethyl acetate) was dissolved in dilute sodium carbonate, mixed with much powdered ice, and then a 1 per cent. solution of permanganate slowly run in, the whole being vigorously stirred by a turbine. The colour of the permanganate disappeared instantly at first, and, when no further reduction took place and the pink colour remained, the excess was removed by adding a little sodium sulphite and the whole heated to boiling.

The filtrate and washings of the manganese precipitate were evaporated to a small bulk, acidified, saturated with ammonium sulphate, and allowed to remain for two days, when a crystalline acid separated in quantity. This was collected, recrystallised from water, and the stout needles thus obtained analysed, with the following result:

0·1341 gave 0·2714 CO_2 and 0·0617 H_2O. C = 55·2; H = 5·1.

$C_{11}H_{12}O_6$ requires C = 55·0; H = 5·0 per cent.

This acid melted at 214—215°, and was found to be *2-carboxy-4:5-dimethoxyphenylacetic acid* (Trans., 1902, **81**, 1028; 1907, **91**, 1082).

The authors wish to state that much of the very heavy expense entailed in carrying out these experiments has been met by repeated grants from the Government Grant Committee of the Royal Society and from the Chemical Society.

THE UNIVERSITY,
MANCHESTER.

XLVII.—*The Crystal Form of Halogen Derivatives of Open-chain Hydrocarbons with Reference to the Barlow-Pope Theory of Structure.*

By FRANS MAURITS JAEGER, Ph.D.

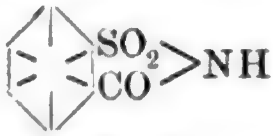
THE results of a series of crystallographic investigations detailed below furnish a striking demonstration of the power which the Barlow-Pope theory gives us of foreseeing those geometrical analogies which, according to the theory (Trans., 1906, **89**, 1675; 1907, **91**, 1150), should exist between the crystalline forms of constitutionally-related substances. A direct indication is thus obtained of the correctness of Barlow and Pope's fundamental hypothesis which can be denied only by those who attribute to the theory too wide a scope or who make for it claims which do not result from its premises. The theory is not to be regarded as affording an explanation of valency, as a substitute for the theory of structure of organic chemistry, nor as furnishing an indication of the occurrence or non-occurrence of miscibility among solid phases. In my opinion, its value lies in the fact that it enables us, by means of a simple hypothesis, to foresee the geometrical forms and parameters of crystalline substances, and to point out beforehand the geometrical relationships existing between certain substitution derivatives of homologous series.

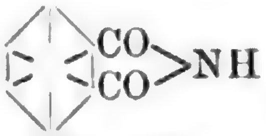
If applied within the limits just defined, the theory is, I think, capable of rendering very valuable service in connexion with chemico-crystallographic investigation. That the possibility of unlimited miscibility in the solid state does not necessarily follow from the geometrical relationships resulting from the application of the theory, appears from the established fact that the halogen derivatives of hydrocarbons discussed in the present paper exhibit extremely slight or no miscibility, although their crystalline forms are very closely related.

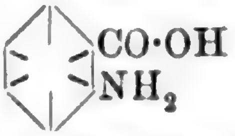
Similarly, the new theory does not explain the difference in velocity of growth in corresponding directions exhibited by all these substances. The single fact, however, that the geometrical analogies which the theory indicates as existing between the substances dealt with have been experimentally discovered, is a striking proof of the correctness of the principles on which it is based.

As instances of the occurrence of crystallographic analogy between related substances which differ in valency volume by an even number of units, Barlow and Pope have quoted, amongst others, the known similarity in crystalline form between calcite and sodium nitrate and between aragonite and potassium nitrate (Trans., 1906, **89**, 1732). To these instances, I would add the following. The hexagonal iodoform, CHI_3, with $a : c = 1 : 1{\cdot}1084$ (Pope, Trans., 1899, **75**, 46), and phosphorus tri-iodide, with $a : c = 1 : 1{\cdot}1009$ (Nordenskiöld, *Bihang K. Svenska Vet.-Akad. Handl.*, 1874, **2**, 2), show a close crystallographic resemblance, as Bruni has already remarked (Ahrens' *Vorträge*, 1901, **6**, 44), and are related through the second geometrical property stated by Barlow and Pope; I have found, further, that the two substances are miscible to a considerable extent one with the other in the solid state. The same kind of morphotropic relationship indicated by the theory exists between benzylideneaniline and stilbene and between dibenzyl and benzylaniline (Jaeger, *Proc. K. Akad. Wetensch. Amsterdam*, 1905, **8**, 466).

A further case of the same kind may be briefly described. From the theory, it is to be foreseen that analogy of form should exist between:


Saccharin.


Phthalimide.


Anthranilic acid.

Between the first two, in which the groups $\cdot SO_2 \cdot$ and $\cdot CO \cdot$, both of valency volume 6, are interchanged, the relationship should be very distinct, whilst anthranilic acid should be less closely related to them; the latter substance should, indeed, be related to the former much as *o*-sulphobenzoic acid is related to its two chlorides (Barlow and Pope, Trans., 1906, **89**, 1734).

After many fruitless attempts, I succeeded in obtaining phthalimide in very lustrous, colourless needles belonging to the monosymmetric prismatic system (*Zeitsch. Kryst. Min.*, 1907, **44**, 61). The axial ratios are:

$$a : b : c = 1{\cdot}4913 : 1 : 0{\cdot}4967,\ \beta = 91^\circ 18' 40'',$$

and there is a very perfect cleavage on {100}.

The corresponding values for saccharin are:

$$a:b:c=1 \cdot 3565:1:0 \cdot 4298,\ \beta=94^\circ 3',$$

and there is also a perfect cleavage on {100}. These two substances thus exhibit a remarkably close morphotropic relationship.

Anthranilic acid crystallises in the orthorhombic bipyramidal system with $a:b:c=0 \cdot 5959:1:1 \cdot 2901$ (Haushofer, *Zeitsch. Kryst. Min.*, 1879, 1, 505), and my own measurements confirm these axial ratios. For the calculation of the equivalence parameters, $3c/2$ is taken, just as was done in the case of saccharin by Barlow and Pope. The table of equivalence parameters of substances related to saccharin given by these authors (*loc. cit.*, p. 1734) can now be completed by the following additions:

	x : y : z.
Saccharin	2·5183 : 3·6857 : 4·7521
Phthalimide	2·4623 : 3·3022 : 4·9197
Anthranilic acid	2·2612 : 3·7945 : 4·8952

A complete verification of the facts foreseen by the aid of the new theory is thus obtained by the experimental study of this series of substances.

The crystallographic results detailed below, obtained by the examination of a number of halogen derivatives of aliphatic hydrocarbons, speak even more strongly than the above in favour of the theory. In accordance with Barlow and Pope's method of formulation, the assemblage representing methane should, by operations carried out with the aid of the first and second geometrical properties, be convertible into the assemblage representing any halogen derivative of any open-chain hydrocarbon. These operations, further, should be comparatively simple ones, so that, without discussing the precise form of the assemblage in each individual case, it would be anticipated that close morphotropic relationships should exist between the substances in question.

Prof. van Romburgh has been kind enough to supply me with the three bromine additive products of the triply unsaturated 1:3:5-hexatriene, $CH_2{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH_2$; of these, I have measured the crystals of the di- and tetra-bromide, but have not yet succeeded in obtaining the hexabromide in measurable form. I have also measured crystals of tetraiodoethylene, C_2I_4, and the symmetrical tetrabromo-$\beta\beta$-dimethylpropane, $C(CH_2Br)_4$. All these substances, as the theory indicates, exhibit very close morphotropic relationships, although considerable differences in external habit are to be noted.

In accordance with the symmetrical character of the methane molecule, the assemblage representing this hydrocarbon must possess cubic marshalling; consequently, it is found that carbon tetraiodide crystallises in the cubic system. The cubic marshalling of the cubic assemblage should be retained if such a substitution is performed on it as converts it into the assemblage representing $\beta\beta$-dimethylpropane; it is therefore to be expected that tetrabromo-$\beta\beta$-dimethylpropane would crystallise in a cubic or a pseudo-cubic form, in addition to presenting morphotropic relationships to other fatty halogen derivatives which would themselves not be expected to exhibit cubic marshalling.

Tetrabromo-ββ-dimethylpropane.

Tetrabromo-$\beta\beta$-dimethylpropane, melting at 163°, crystallises from light petroleum in small, colourless needles possessing a penetrating, unpleasant odour. The crystals do not yield very good measurements, and are frequently twinned on {100}, just as the crystals of tetraiodoethylene are often twinned on {001}. The form {100} is predominant and very lustrous, *c*{001} and *r*{$\bar{1}$02} are about equally developed and give good reflections, whilst *q*{012} is small.

Crystal system: monosymmetric prismatic:

$$a : b : c = 2{\cdot}2766 : 1 : 3{\cdot}6486,\ \beta = 67°7'30'':$$

Angle.	Measured.	Calc.
$a : c = 100 : 001$	= 67° 7′30″	—
$c : q = 001 : 012$	= 59 15 0	—
$c : r = 001 : \bar{1}02$	= 46 44 30	—
$a : r = 100 : \bar{1}02$	= 65°56′	66° 8′0″
$a : q = 100 : 012$	= 78 44	78 33 0

The extinction in the orthodiagonal zone is normally orientated, but the optic axial plane could not be determined. The density of the crystals was determined as 2·596 at 15°; the molecular volume is thus 149·39 and the topic parameters:

$$\chi : \psi : \omega = 6{\cdot}1297 : 2{\cdot}6925 : 9{\cdot}8239.$$

If in the above description the observed forms are so altered in indices that {100}, {001}, {$\bar{1}$02}, and {012} become {100}, {102}, {$\bar{1}$02}, and {112} respectively, the axial ratios become:

$$a : b : c = 1{\cdot}0484 : 1 : 0{\cdot}9472,\ \beta = 90°44'50'',$$

and at the same time the distribution of forms becomes somewhat more symmetrical. From this mode of regarding the crystal form, it is distinctly seen to be pseudo-cubic, as was anticipated from the mode in which the corresponding assemblage must be derived from that of methane.

On crystallising the substance from benzene, beautiful crystals of glassy lustre separate, which have the composition $C(CH_2Br)_4,C_6H_6$; these belong to the anorthic pinacoidal system, but could not be completely measured, owing to the rapidity with which efflorescence occurs. It was, however, established that the zone parallel to the longer direction of the crystals contains almost the same angles as the plane of symmetry zone in the crystals of the pure substance. This suggests that the benzene becomes introduced into the molecular structure as a layer lying parallel to the form {010} in the monosymmetric crystals (compare Barlow and Pope, Trans., 1906, **89**, 1685); it is noteworthy that the two constituents of the anorthic crystals have approximately the same valency volume, namely, 32 and 30.

Fedoroff has shown (*J. pr. Chem.*, 1890, [ii], **42**, 145) that the symmetrical tetrabromobutane, $CH_3 \cdot CBr_2 \cdot CBr_2 \cdot CH_3$, melting at 230°, crystallises in a stable tetragonal form, with $a:c=1:1{\cdot}28$, and a labile orthorhombic form; the axial ratios of the latter are $a:b:c=1{\cdot}8671:1:3{\cdot}478$ if the forms observed by Fedoroff are taken as {110} and {012}. The labile form is stable at −10°, and its morphotropic relationship to tetrabromo-*ββ*-dimethylpropane is at once obvious.

1 : 3 : 5-*Hexatriene Dibromide.*

This substance was first, but erroneously, described by Griner (*Ann. Chim. Phys.*, 1892, [vi], **26**, 381) as anorthic. The compound prepared by van Romburgh and van Dorssen (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, **9**, 111) by two different methods gave identical results; it melts at 86·5—87°, and apparently has the constitution $CH_2{:}CH \cdot CHBr \cdot CHBr \cdot CH{:}CH_2$. The crystals deposited from a mixture of ether and light petroleum consist of large, slightly yellow prisms or thin needles; they are very lustrous, but soon become blackened as the result of polymerisation on exposure to light. The crystals possess a penetrating, but not unpleasant, lemon-like odour; they often yield anomalous angular measurements, but some are geometrically quite simple. The forms *c*{001} and *a*{100} are about equally developed, and, in general, the crystals are flattened on {001}; *o*{111} is large and lustrous, *s*{101} is small, and *r*{$\bar{1}01$} is larger and gives better reflexions. The crystal habit is elongated in the direction of the axis *b*, and the orthodiagonal zone frequently exhibits vicinal faces of which the indices could not be determined. No definite cleavage was observed.

Crystal system: monosymmetric prismatic:

$$a:b:c=2{\cdot}9021:1:3{\cdot}3330,\ \beta=64^\circ 40' 30'':$$

Angle.	Measured.	Calc.	Angle.	Measured.	Calc.
$a:c=100:001$	$=64^\circ 40' 30''$	—	$a:s=100:101$	$=34^\circ\ 6'\ 0''$	$33^\circ 51'\ 0''$
$a:r=100:10\bar{1}$	$=51\ 28\ 30$	—	$o:r=111:10\bar{1}$	$=94\ 48\ \ 0$	$94\ 28\ 30$
$o:c=111:001$	$=64\ 54\ 30$	—	$o:o=111:\bar{1}1\bar{1}$	$=62\ 18\ \ 0$	$62\ 13\ \ 0$
$a:o=100:111$	$=63\ 27\ \ 0$	$63^\circ 22'\ 0''$	$c:r=001:\bar{1}01$	$=63\ 56\ 30$	$63\ 51\ \ 0$
$c:s=001:101$	$=34\ 34\ 30$	$34\ 39\ 30$	$s:o=101:111$	$=58\ 50\ 30$	$58\ 53\ 30$

Very strong conical refraction is observed through {100} and {001}; the optic axial plane is (010), and one optic axis emerges almost perpendicularly through (001). The crystals show very strong inclined dispersion with $\rho < v$; the double refraction is positive in sign. The density of the crystals is approximately 2·131 at 18°, but the potassium mercuric iodide solution used appears slightly to attack the material. The molecular volume is thus 112·7, and the topic parameters are:

$$\chi : \psi : \omega = 6{\cdot}8040 : 2{\cdot}3445 : 7{\cdot}8143.$$

For comparison with the latter values, the data for *p*-dibromobenzene may be quoted; Boeris describes this substance as monosymmetric with $a : b : c = 2{\cdot}6660 : 1 : 2{\cdot}8358$, $\beta = 67°22'$ (*Atti R. Accad. Lincei*, 1899, **8**, ii, 184). The density is 2·220, so that the molecular volume is 106·3 and the topic parameters:

$$\chi : \psi : \omega = 6{\cdot}6090 : 2{\cdot}4790 : 7{\cdot}0299.$$

1 : 3 : 5-*Hexatriene Tetrabromide.*

This substance was prepared by van Romburgh and van Dorssen (*loc. cit.*) by the action of bromine on the hydrocarbon in chloroform solution under the influence of sunlight; it melts at 114—115°, and probably possesses the constitution

$$CH_2Br{\cdot}CHBr{\cdot}CHBr{\cdot}CHBr{\cdot}CH{:}CH_2.$$

The crystals deposited from a mixture of ethyl acetate and methyl alcohol consist of small, colourless needles. The forms $m\{110\}$ and $a\{100\}$ are about equally developed, $c\{001\}$ is small, but easily measurable, and $r\{\bar{1}02\}$ is very small and often absent. The crystals are striated in the direction of the *c*-axis, and are frequently flattened upon two parallel faces of $m\{110\}$. The ratio $b : c$ could be only approximately determined. No distinct cleavage was observed.

Crystal system: monosymmetric prismatic:

$$a : b : c = 3{\cdot}1917 : 1 : 3{\cdot}635, \beta = 69°1' :$$

Angle.	Measured.	Calc.	Angle.	Measured.	Calc.
$c : m = 001 : 110$	$= 83°27'30''$	—	$a : c = 100 : 001$	$= 68\ 59'$	69° 1'
$a : m = 100 : 100$	$= 71\ 27\ \ 0$	—	$m : m = 110 : \bar{1}10$	$= 37\ \ 4$	37 4
$c : r = 001 : \bar{1}02$	$= 33\ 44\ \ 0$	—	$a : r = 100 : 10\bar{2}$	$= 77\ 14$	77 15

The extinction upon {100} is straight, and upon {110} inclined at about 52½° to the direction of the *c*-axis. The optic axial plane is (010), and the dispersion is inclined. One optic axis is visible through {100} at the edge of the microscope field. The density of the crystals is 2·362 at 15°; the molecular volume is thus 169·35, and the topic parameters:

$$\chi : \psi : \omega = 7{\cdot}9807 : 2{\cdot}5005 : 9{\cdot}0892.$$

The crystals show in their axial ratios a close morphotropic relationship with the corresponding dibromide, and the topic parameters indicate that the molecular distances change considerably in the directions *a* and *c*, and but slightly in the direction of the *b*-axis.

If, in the above description, the indices of the forms $\{100\}$, $\{001\}$, $\{\bar{1}02\}$, and $\{110\}$ are changed to the more symmetrical forms $\{100\}$, $\{\bar{1}01\}$, $\{101\}$, and $\{110\}$ respectively, the axial ratios become:

$$a:b:c=3{\cdot}0445:1:0{\cdot}9668,\ \beta=86°15'50''.$$

The morphotropic relation of the substance to normal hexane is seen if, in Negri's description of the orthorhombic tetrabromohexane,

$$CH_2Br{\cdot}CHBr{\cdot}CH_2{\cdot}CH_2{\cdot}CHBr{\cdot}CH_2Br,$$

in which $a:b:c = 0{\cdot}36408:1:0{\cdot}37882$ (*Ber.*, 1889, **22**, 2498), an interchange of axes is made which throws them into the form of $b:c:a$. The axial ratios are then obtained in the form:

$$a:b:c=2{\cdot}6398:1:0{\cdot}9611,\ \beta=90°,$$

values which are very similar to the transposed form of those for the hexatriene tetrabromide.

Tetraiodoethylene, C_2I_4.

This substance, melting at 188°, crystallises from a mixture of benzene, light petroleum, and a little alcohol in pale yellow, flat, lustrous needles. Most, although not all, of the crystals are twinned on $c\{001\}$, and this plane is also a direction of perfect cleavage. The form $c\{001\}$ is the largest, and gives perfect reflexions; $r\{\bar{1}01\}$ and $r'\{\bar{2}01\}$ are small and about equally developed, and also give good reflexions. The form $o\{111\}$ is large and lustrous, and occasionally indications of the form $\{225\}$ are observed. The crystals are elongated in the direction of the b-axis, and are flattened upon $\{001\}$. The etch-figures produced by α-monobromonaphthalene are in accordance with the symmetry adopted.

Crystal system: monosymmetric prismatic:

$$a:b:c=2{\cdot}9442:1:2{\cdot}4387,\ \beta=70°44'30'':$$

Angle.	Measured.	Calc.	Angle.	Measured.	Calc.
$a:c=100:001$	$=70°44'30''$	—	$c:r=001:\bar{1}01$	$=60°52'30''$	$60°52'30''$
$c:o=001:\bar{1}11$	$=79\ 50\ 30$	—	$r:r'=\bar{1}01:\bar{2}01$	$=23\ 11\ \ 0$	$23\ 11\ \ 0$
$c:r'=001:\bar{2}01$	$=84\ \ 3\ 30$	—	$o:r=\bar{1}11:\bar{1}01$	$=68\ 46\ 30$	$68\ 45\ 30$
$o:o=\bar{1}11:11\bar{1}$	$=42\ 27\ \ 0$	$42°29'30''$	$o:a=11\bar{1}:100$	$=76\ 13\ \ 0$	$76\ \ 4\ \ 0$

The extinction in the orthodiagonal zone is normally orientated, but the optic axial plane could not be determined. The density of the crystals is 2·983 at 20°; the molecular volume is thus 169·66, and the topic parameters are $\chi:\psi:\omega=7{\cdot}6803:2{\cdot}6087:8{\cdot}9701$.

In the case of this substance, also, a close morphotropic relationship is observable with the preceding halogen derivatives.

As a result of the foregoing investigation, it is to be concluded that the analogies of crystalline form amongst the substances concerned, which are indicated by the theory of Barlow and Pope, have actually been observed.

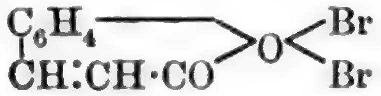
ZAANDAM,
HOLLAND.

XLVIII.—*The Residual Affinity of the Coumarins and Thiocoumarins as shown by their Additive Compounds.*

By ARTHUR CLAYTON, B.Sc.

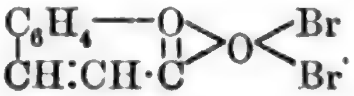
COUMARIN, the lactone of *o*-coumaric acid, possesses in a marked degree the property of yielding additive compounds with reagents of very diverse types, and in this respect is distinguished from the lactones in general, which do not as a class exhibit this feature to any great extent.

The earliest known additive compound of coumarin was the dibromide discovered by Sir W. H. Perkin (*Annalen*, 1871, **157**, 116), and afterwards again examined by Ebert (*Annalen*, 1884, **226**, 348). The results obtained by these investigators render it certain that the bromine is attached, not to the carbon atoms united by unsaturated linking, but either to the oxidic or the ketonic oxygen. This is shown by the ease with which the halogen is entirely eliminated. If the ordinary lactonic constitution for coumarin be accepted, this dibromide might be represented by formula I, whilst the alternative configuration suggested by Morgan and Micklethwait (Trans., 1906, **87**, 868) would lead to formula II:



$$\begin{matrix} C_6H_4\text{———}\\ CH{:}CH\cdot CO \end{matrix}\!>\!O\!<\!\begin{matrix} Br \\ Br \end{matrix}$$

I.



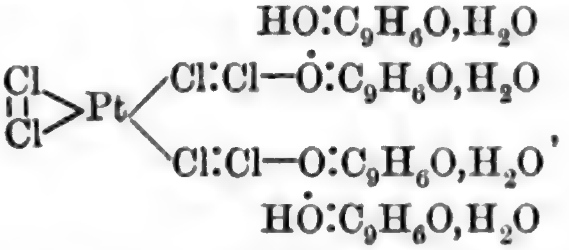
$$\begin{matrix} C_6H_4\text{—}O \\ CH{:}CH\cdot C \end{matrix}\!>\!O\!<\!\begin{matrix} Br \\ Br \end{matrix}$$

II.

Coumarin combines additively with the metallic oxides and hydroxides, as was shown long ago by R. Williamson (*Jahresber.*, 1875, 587), these compounds generally conforming to the types $C_9H_6O_2,2ROH$ and $C_9H_6O_2,R_2O$, where R is an alkali metal. The next observation of the combining proclivities of coumarin is due to Ebert, who found (*loc. cit.*) that the lactone dissolved easily in concentrated hydrobromic acid, the solution furnishing a hydrobromide, which, however, was so unstable that it could only be preserved at low temperatures, and was therefore not analysed.

By employing concentrated hydrochloric acid as the solvent and then adding a strong solution of chloroplatinic acid, Morgan and

Micklethwait (*ibid.*, p. 863) obtained a crystalline platinichloride, $4C_9H_6O_2,H_2PtCl_6,4H_2O$, to which they gave the graphic formula



where C_9H_6O is the coumarin residue, excluding the oxygen atom, which becomes quadrivalent in the formation of the double salt. These authors (*loc. cit.*) also obtained a cobalticyanide of a more normal type, which has a composition corresponding with the formula $3C_9H_6O_2,H_3Co(CN)_6,3H_2O$.

In the experiments described in this paper, the investigation has been extended to the homologues and the sulphur analogues of coumarin, and in most cases it has been found possible to demonstrate the existence of additive compounds, either of the oxonium types or produced by the union of the lactone itself with a metallic salt.

Coumarin and Thiocoumarin.

Coumarin Mercurichloride.—Coumarin and mercuric chloride in equimolecular proportion were dissolved in the smallest possible quantity of ether and mixed together. On leaving the mixture for one or two days, the mercurichloride separated in long, colourless needles which melted at 164—165°:

0·8590 gave 0·5782 AgCl. Cl = 16·65.
0·6381 „ 0·3712 HgS. Hg = 46·84.
$C_9H_6O_2Cl_2Hg$ requires Cl = 17·03; Hg = 47·96 per cent.

Recrystallisation was not found to be advisable, as the affinity between the generators is so slight that dissociation readily occurs. As an instance of the feebleness of the union, it was found that aniline mercurichloride slowly separated on mixing ethereal solutions of aniline and coumarin mercurichloride.

Thiocoumarin, prepared by Tiemann's method (*Ber.*, 1886, **19**, 1661), is generally obtained in dark brown needles, rather difficult to purify by recrystallisation. The substance can, however, readily be purified by boiling its benzene solution for several hours with copper powder and subsequently crystallising from alcohol, when it possesses a brilliant, golden-yellow colour. This method of purification increases the yield of pure thiocoumarin from 50 to 80 per cent. (compare Tiemann, *loc. cit.*).

Thiocoumarin mercurichloride was prepared by mixing an equimolecular proportion of thiocoumarin and mercuric chloride in ethereal solution. A yellow powder immediately separated, and the liquid became quite colourless. The mercurichloride is very insoluble in ordinary solvents, boiling nitrobenzene being the only liquid which appears to exert any solvent action. The substance is decomposed when suspended in water and treated with hydrogen sulphide, thiocoumarin being liberated. On analysis, the mercurichloride gave numbers approximating to those required by the formula

$$C_9H_6OS,HgCl_2.$$

*7-Methylcoumarin and 7-Methylthiocoumarin.**

7-Methylcoumarin Mercurichloride.—The combination of the generators of this substance resulted from their admixture in ethereal solution. As in the case of coumarin mercurichloride some time elapses before crystallisation sets in, attempts at rapid crystallisation always resulting in the separation of an impure product. When once the compound has been prepared, however, crystallisation may be effected much more rapidly. It forms long, colourless needles soluble in ether, benzene, chloroform, and to some extent in water, and from each of these solvents the substance may be recovered unchanged, but, being even more unstable than coumarin mercurichloride, recrystallisation was not found useful as a means of purification. The crystals first formed melted very definitely at 170°:

0·4099 gave 0·2575 AgCl. Cl = 15·54.

$C_{10}H_8O_2Cl_2Hg$ requires Cl = 16·47 per cent.

7-Methylcoumarin Cobalticyanide.—One gram of 7-methylcoumarin was dissolved in concentrated hydrochloric acid; the solution was cooled as rapidly as possible to prevent crystallisation, and then added to an excess of cobalticyanic acid prepared according to von Baeyer and Villiger's directions (*Ber.*, 1901, **34**, 2687). The compound separated as a white, crystalline powder, and after several days the mother liquor yielded colourless cubes of the same substance. After filtration, the powder was washed with dilute hydrochloric acid, and dried at the ordinary temperature as water of crystallisation was evolved at 100°:

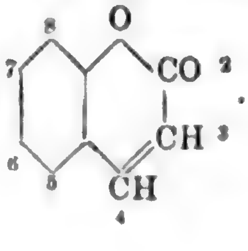
0·6456 gave 0·1058 H_2O. H_2O = 16·39.

0·8030 „ 0·1118 Co. Co = 13·92.

$C_{10}H_8O_2,H_3Co(CN)_6,4H_2O$ requires H_2O = 16·00; Co = 13·11 per cent.

7-Methylcoumarin platinichloride was not prepared in the pure state,

---

* In this paper the notation is in accordance with the numbering indicated in the formula  .

but on mixing concentrated solutions of 7-methylcoumarin and chloroplatinic acid in concentrated hydrochloric acid, yellow crystals containing platinum separated. These were instantly decomposed by moisture.

7-*Methylthiocoumarin.*—The preparation of this compound was effected by heating an intimate mixture of equal weights of 7-methylcoumarin and phosphorus pentasulphide to 120° in a paraffin-bath until the mixture had been molten for seven minutes. The powdered mass, after extraction with benzene and subsequent crystallisation from alcohol, was treated with copper powder, and then appeared as glistening, golden-yellow leaflets melting at 125—126°:

0·1664 gave 0·2243 $BaSO_4$. S = 18·51.

$C_{10}H_8OS$ requires S = 18·18 per cent.

On shaking a solution of the thiocoumarin in benzene with yellow mercuric oxide, 7-methylcoumarin was regenerated, thus proving the constitution of the substance.

7-*Methylcoumarinoxime.*—This substance was obtained by heating equal molecules of sodium hydroxide, 7-methylthiocoumarin, and hydroxylamine hydrochloride in alcoholic solution for two days. The product, when poured into water, yielded an emulsion which soon furnished the solid oxime. This was collected and crystallised from boiling water, from which it separated in white needles melting at 178°:

0·2664 gave 17·85 c.c. nitrogen at 20° and 773 mm. N = 7·77.

$C_{10}H_9O_2N$ requires N = 8·00 per cent.

The substance is less soluble in water than coumarinoxime.

7-*Methylcoumarinphenylhydrazone.*—An alcoholic solution of equal molecules of 7-methylthiocoumarin and phenylhydrazine was boiled until no more hydrogen sulphide was evolved, the operation requiring about four days. On cooling the solution, yellowish-brown needles were obtained, which, after three crystallisations from alcohol, melted at 139°:

0·2635 gave 25·8 c.c. nitrogen at 20° and 773 mm. N = 11·36.

$C_{16}H_{14}ON_2$ requires N = 11·20 per cent.

7-*Methylcoumarin mercurichloride*, prepared in the same way as coumarin mercurichloride, was obtained as a yellow powder very similar to the latter substance:

0·5207 gave 0·3439 AgCl. Cl = 16·34.

$C_{10}H_8OSCl_2Hg$ requires Cl = 15·88 per cent.

The compound decomposes without melting, and regenerates 7-methylthiocoumarin when treated with hydrogen sulphide.

4 : 7-*Dimethylcoumarin and* 4 : 7-*Dimethylthiocoumarin.*

4 : 7-*Dimethylcoumarin Mercurichloride.*—The combination of mercuric chloride and 4 : 7-dimethylcoumarin was effected by a method similar to that used for the preparation of 7-methylcoumarin mercurichloride. The substance, which was produced more readily and more plentifully than the latter compound, forms beautiful, white needles, crystals two inches and more in length being easily obtained. Its behaviour towards solvents is very similar to that of 7-methylcoumarin mercurichloride, and although more stable than this compound it appears in its purest form before crystallisation, when it melts very definitely at 175°. Two or three crystallisations did not noticeably change the melting point:

0·7226 gave 0·4414 AgCl. Cl = 15·12.
0·4855 „ 0·2456 HgS. Hg = 43·61.
$C_{11}H_{10}O_2Cl_2Hg$ requires Cl = 15·95; Hg = 44·94 per cent.

4 : 7-*Dimethylcoumarin cobalticyanide* was obtained by adding a solution of 4 : 7-dimethylcoumarin in concentrated hydrochloric acid to an excess of cobalticyanic acid in the same solvent. The white, microcrystalline product was much more easily and plentifully obtained than the corresponding compound of 7-methylcoumarin. As it could not be recrystallised without decomposition, the substance was washed with dilute hydrochloric acid and dried. It was found to lose weight at 100°, and in order to prove that this loss was due to the elimination of water and not to the evolution of gases containing nitrogen, the cobalt was estimated in the substance before heating and the nitrogen after three hours' heating in a steam-oven:

0·8784 gave 0·0908 H_2O. H_2O = 15·72.
0·6331 „ 0·0815 Co. Co = 12·87.
$C_{11}H_{10}O_2,H_3Co(CN)_6,4H_2O$ requires H_2O = 15·52; Co = 12·72 per cent.

0·2103 of the anhydrous substance gave 40·0 c.c. nitrogen at 21° and 757 mm. N = 21·64.
$C_{11}H_{10}O_2,H_3Co(CN)_6$ requires N = 21·43 per cent.

4 : 7-*Dimethylcoumarin platinichloride* was not obtained in the pure state, but yellow crystals were formed which melted indefinitely between 160° and 170°, and on analysis were found to contain 22·5 per cent. of platinum. The oxonium salt was immediately decomposed by water, and even by concentrated hydrochloric acid, with the liberation of 4 : 7-dimethylcoumarin, but was recrystallised from a concentrated solution of platinic chloride in the latter solvent. Since it was not found possible to wash the crystals without decomposing them, data for the establishment of a formula could not be obtained.

4 : 7-*Dimethylthiocoumarin* resulted when 4 : 7-dimethylthiocoumarin was subjected to the same treatment as that employed for the conversion of 7-methylcoumarin into its sulphur analogue ; it crystallised from alcohol in dark needles which, after eleven crystallisations, were obtained with a greenish-yellow colour, which was not noticeably changed by treatment with copper powder. Like its homologues, it yields the corresponding coumarin when treated with yellow mercuric oxide. The pure substance melts at 118—119° :

0·3045 gave 0·3789 $BaSO_4$. S = 17·09.

$C_{11}H_{10}OS$ requires S = 16·80 per cent.

It was noticed throughout that there was a strong tendency for the thiocoumarins to give on analysis a high percentage for sulphur, and that this extra sulphur was retained with considerable persistency through several successive crystallisations. This property was especially marked in the case of 4 : 7-dimethylthiocoumarin, which after three crystallisations from alcohol yielded 21 per cent. of sulphur, thus making it appear likely that the sulphur is united to the thiocoumarin by some weak affinity. These loosely combined sulphur compounds can generally be removed by the treatment with copper powder mentioned on page 525.

4 : 7-*Dimethylcoumarinoxime* was obtained by the same method as that used for the preparation of 7-methylcoumarinoxime ; it is less soluble in water than the latter compound, but separates from a mixture of alcohol and water in fine, white needles melting at 179° :

0·3377 gave 21·4 c.c. nitrogen at 19° and 748 mm. N = 7·17.

$C_{11}H_{11}O_2N$ requires N = 7·41 per cent.

4 : 7-*Dimethylcoumarinphenylhydrazone*, prepared in the same manner as 7-methylcoumarinphenylhydrazone, forms golden-brown needles melting at 99—100° :

0·1947 gave 18·8 c.c. nitrogen at 22° and 762 mm. N = 10·97.

$C_{17}H_{16}ON_2$ requires N = 10·61 per cent.

4 : 7-*Dimethylthiocoumarin Mercurichloride*.—The addition of the generators of this substance is effected by their admixture in ethereal solution. The product forms a yellow, amorphous powder with great readiness, and behaves towards solvents like thiocoumarin mercurichloride. Hydrogen sulphide regenerates 4 : 7-dimethylthiocoumarin :

0·1466 gave 0·0934 AgCl. Cl = 15·78.

$C_{11}H_{10}OSCl_2Hg$ requires Cl = 15·40 per cent.

3 : 4 : 7-*Trimethylcoumarin and* 3 : 4 - 7-*Trimethylthiocoumarin.*

3 : 4 : 7-*Trimethylcoumarin mercurichloride*, obtained by the general method of preparation, separated from ether in a rather ill-defined,

felt-like mass, totally different in appearance from the other mercurichlorides. Analysis gave numbers which approximated to those required by the formula $C_{12}H_{12}O_2.HgCl_2$.

3 : 4 : 7-*Trimethylcoumarin cobalticyanide* was obtained with some difficulty by the method already employed, and presented the same features as the other cobalticyanides, being difficult to obtain in a state approaching purity. Data were obtained which indicated the formula $C_{12}H_{12}O_2,H_3Co(CN)_6$ for the anhydrous substance.

3 : 4 : 7-*Trimethylcoumarin platinichloride* was not prepared in the pure state, but indications of its existence were obtained.

3 : 4 : 7-*Trimethylthiocoumarin.*—The preparation of this substance proceeded smoothly by the general method, the compound being finally obtained in very brilliant reddish-yellow needles melting at 124—125°:

0·3114 gave 0·3731 $BaSO_4$. S = 16·46.

$C_{12}H_{12}OS$ requires S = 15·69 per cent.

The product has the general properties and solubilities of the thiocoumarins.

3 : 4 : 7-*Trimethylcoumarinoxime* results from the interaction of equimolecular proportions of 3 : 4 : 7-trimethylthiocoumarin, sodium hydroxide, and hydroxylamine hydrochloride. It is much less soluble than 4 : 7-dimethylcoumarinoxime, but crystallises from alcohol in needles melting at 198°:

0·2099 gave 11·4 c.c. nitrogen at 9° and 770 mm. N = 6·61.

$C_{12}H_{13}O_2N$ requires N = 6·89 per cent.

3 : 4 : 7-*Trimethylcoumarinphenylhydrazone* was obtained in beautiful yellow needles by the general method of preparation. It may be crystallised from alcohol, and melts at 135°:

0·2020 gave 18·3 c.c. nitrogen at 19° and 733 mm. N = 10·02.

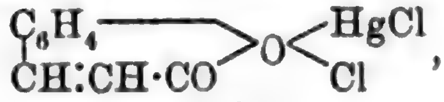
$C_{18}H_{18}ON_2$ requires N = 10·07 per cent.

General Conclusions.

(1) The homologues of coumarin may be converted into the corresponding thiocoumarins by treatment with phosphorus pentasulphide and these thiocoumarins, when purified from adherent sulphur compounds, exhibit a distinct yellow colour, in this respect differing from the coumarins which are colourless.

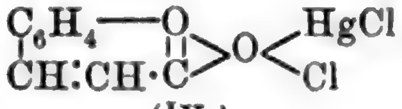
(2) Coumarin and its homologues and its sulphur analogues give rise to additive compounds with mercuric chloride in which the reagents combine in molecular proportion. In the case of the oxy-

compounds, one of the following formulæ (III and IV) may be adopted.



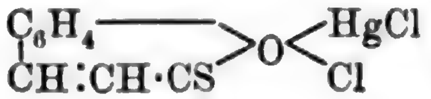
$$\begin{array}{l}C_6H_4\text{———}\\CH{:}CH{\cdot}CO\end{array}\!\!>O<\!\!\begin{array}{l}HgCl\\Cl\end{array},$$

(III.)



$$\begin{array}{l}C_6H_4\text{—}O\\CH{:}CH{\cdot}C\end{array}\!\!>O<\!\!\begin{array}{l}HgCl\\Cl\end{array}$$

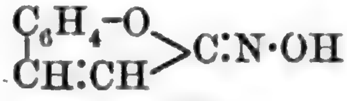
(IV.)



$$\begin{array}{l}C_6H_4\text{———}\\CH{:}CH{\cdot}CS\end{array}\!\!>O<\!\!\begin{array}{l}HgCl\\Cl\end{array}.$$

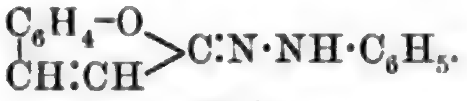
(V.)

(3) In the case of the thiocoumarins, it is probable that a formula of the former type is more appropriate. Thiocoumarin mercurichloride would thus have the constitution indicated by formula V. This view is confirmed by the fact that the thiocoumarins differ from the coumarins in their behaviour towards hydroxylamine and phenylhydrazine. These compounds, although regarded as agents for the detection of the carbonyl group, do not react with the coumarins (Tiemann, *Ber.*, 1886, **19**, 1663), whereas condensation does occur with the thiocoumarins, leading to the production of the coumarin oximes and the coumarinphenylhydrazones (VI and VII):



$$\begin{array}{l}C_6H_4\text{-}O\\CH{:}CH\end{array}\!\!>C{:}N{\cdot}OH$$

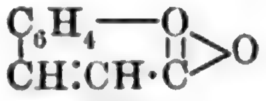
(VI.)



$$\begin{array}{l}C_6H_4\text{-}O\\CH{:}CH\end{array}\!\!>C{:}N{\cdot}NH{\cdot}C_6H_5.$$

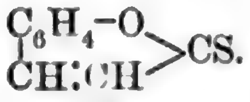
(VII.)

(4) The negative results with the coumarins themselves support the view that in these lactones the ketonic group no longer exists as such, being modified in the sense indicated by formula VIII. On the other hand, the oxime and phenylhydrazone condensation which occurs with the thiocoumarins justifies the belief that the thio-compounds contain the thiocarbonyl group as represented by formula IX:



$$\begin{array}{l}C_6H_4\text{—}O\\CH{:}CH{\cdot}C\end{array}\!\!>O$$

(VIII.)



$$\begin{array}{l}C_6H_4\text{-}O\\CH{:}CH\end{array}\!\!>CS.$$

(IX.)

The marked colour difference between the coumarins and thiocoumarins may also be regarded as subsidiary evidence that they are differently constituted, for the coumarins are all colourless substances, whilst the thiocoumarins without exception have a distinctly yellow or orange colour.

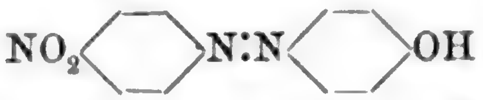
The constitutional formulæ assigned to the additive compounds of the coumarins and thiocoumarins are based on one assumption, namely, that oxygen exhibits quadrivalency, more particularly towards the halogens or towards compounds containing the halogens. This supposition is in accordance with the general behaviour of oxygen and the halogens in both their inorganic and organic compounds.

Royal College of Science, London,
South Kensington.

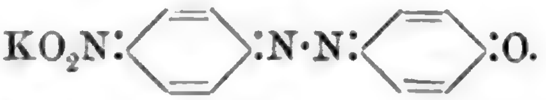
XLIX.—*Colour and Constitution of Azomethine Compounds. Part I.*

By FRANK GEORGE POPE.

IN a paper recently communicated to the Society by Hewitt and Mitchell (Trans., 1907, **91**, 1251), it was shown that the nitroazophenols and naphthols on treatment with alkalis gave salts, which in the case of the para-nitrated compounds exhibit absorptions of a type radically different from that shown by the phenol or naphthol itself, except where a group has been introduced into the molecule which, by virtue of its character and position, prevents the formation of a diquinonoid structure. The authors, considering that a change in the absorption spectrum of a compound when it undergoes transformation into a salt generally points to a radical alteration of constitution, formulate the free azophenols and their alkali salts as follows:

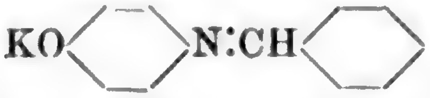


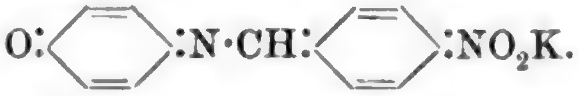
and



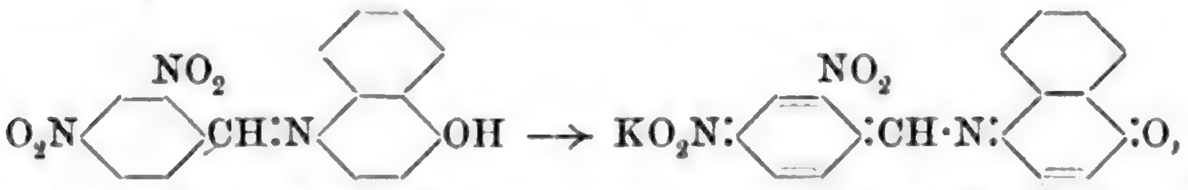
Since the azomethine (·N:CH·) grouping shows a considerable likeness to the azo- (·N:N·) grouping in many respects, it seemed probable that a similar change might be observed in the compounds where such a grouping existed, and this investigation was undertaken to ascertain if such were the case. Very little appears in the current chemical literature concerning the difference between the azomethine compounds and their salts. Möhlau (*Ber.*, 1898, **31**, 2260) has prepared such compounds by the condensation of 5-aminosalicylic acid and the three nitrobenzaldehydes, and has noted that the substances are yellow, and, in the case of the ortho- and para-nitro-compounds, give orange-yellow solutions with sodium hydroxide. Sachs (*Ber.*, 1907, **40**, 3230) has also prepared similar compounds by condensing 2:4-dinitrobenzaldehyde with various aminonaphthols, and has noted that in the cases of the 4:1-, 5:1-, and 8:2-aminonaphthols, on the addition of a caustic alkali, the solutions become deep blue or violet, the free anhydro-substances giving reddish-brown or orange-red solutions in alcohol.

It was found during the course of the present investigation that the absorption spectra of the free azomethine compounds and of their alkali salts were very different in character, and consequently the same assumption is made in the case of the nitrated azomethine compounds as in that of the similarly constituted nitroazophenols, namely, that the transformation of the nitroazomethine structure to the *iso*nitro*iso*azomethine form is accompanied by a change in the oscillation-frequency of the molecule; absorption bands appear in the violet or blue end of the spectrum with the result that the solutions appear red or reddish-brown by transmitted light. This is rendered clear by comparing the absorptions of benzylidene-*p*-aminophenol and 4-nitrobenzylidene-*p*-aminophenol. In alcoholic solution (*N*/100), the violet and blue are absorbed as far as wave-lengths 455 and 482 $\mu\mu$ respectively, but, on the addition of potassium hydroxide, the solution of the former shows absorption extending as far as 473 $\mu\mu$ and the latter as far as 622 $\mu\mu$, being continuous from the ultra-violet into the visible spectrum; moreover, the solution changes from pale orange-yellow to a deep reddish-brown. The potassium salts of these compounds may thus be represented as:



and


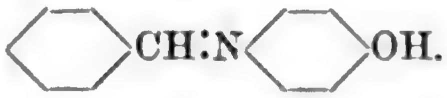
It is to be noted that Sachs' 2′ : 4′-dinitrobenzylidene-4-amino-*a*-naphthol, like *p*-nitrobenzeneazo-*a*-naphthol (Meldola, Trans., 1885, **47**, 661; Bamberger, *Ber.*, 1895, **28**, 848), forms reddish-brown crystals, and gives a deep blue alkaline solution. Consequently, the following formula may be suggested for this compound:



and similar formulæ for the compounds derived from the 5 : 1- and 8 : 2-aminonaphthols, since it is in these positions in the naphthalene nucleus where the possibility of a quinonoid structure is apparent, and, in the 5 : 2- and 7 : 2-aminonaphthol compounds where such a structure is precluded, Sachs found that the solutions in alkali were dark red.

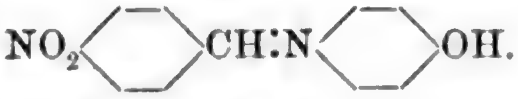
EXPERIMENTAL.

Benzylidene-p-*aminophenol*,



This substance has been previously prepared by Philip (*Ber.*, 1892, **25**, 3248), the melting point being given as 181°. On preparing it by condensing the components in dilute acetic acid, and recrystallising the product from alcohol, it separated in almost colourless needles, melting sharply at 183°. It gives an almost colourless solution in alcohol, which becomes slightly darker (very faintly yellow) on the addition of alkali.

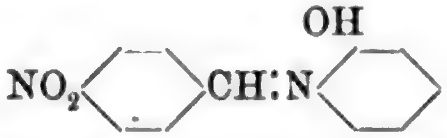
p-*Nitrobenzylidene*-p-*aminophenol*,



Equivalent weights of *p*-nitrobenzaldehyde and of *p*-aminophenol were separately dissolved in dilute acetic acid, the solutions mixed and allowed to stand for some time. The resulting precipitate was crystallised from alcohol, from which small, yellowish-brown needles separated, melting at 168·5°. The substance gives an orange-yellow solution in alcohol, which, on the addition of alkali, becomes a deep orange-red:

0·1612 gave 0·3793 CO_2 and 0·0627 H_2O. C = 64·17; H = 4·32.
$C_{13}H_{10}O_3N_2$ requires C = 64·46; H = 4·13 per cent.

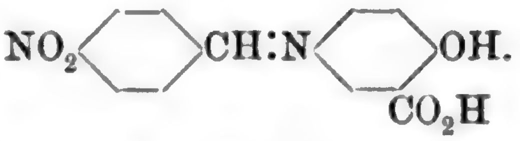
p-*Nitrobenzylidene*-o-*aminophenol*,



This compound was prepared by dissolving equivalent weights of *p*-nitrobenzaldehyde and *o*-aminophenol separately in absolute alcohol and mixing the solutions. Tufts of needles separated after a short time. The compound was precipitated by water and crystallised from alcohol, being obtained in brownish-yellow needles, melting at 161°. Its solution in alcohol is yellow, and on the addition of alkali becomes orange-red:

0·2094 gave 0·4949 CO_2 and 0·0794 H_2O. C = 64·46; H = 4·21.
$C_{13}H_{10}O_3N_2$ requires C = 64·46; H = 4·13 per cent.

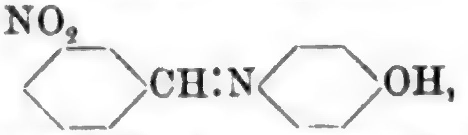
p-*Nitrobenzylidene*-5-*aminosalicylic acid*,



Considerable difficulty was experienced in preparing this substance by the method given by Möhlau (*loc. cit.*), since it was found that a residue containing sodium salts was always left after combustion. The difficulty was overcome by the addition of a small quantity of acetic acid to the solution of 5-aminosalicylic acid hydrochloride in alcohol, and then adding to this the solution of *p*-nitrobenzaldehyde in alcohol (containing the required amount of sodium acetate). The product separated in a few minutes as a brownish-yellow solid, which, when crystallised from dilute alcohol, in which it is somewhat sparingly soluble, melted (with decomposition) at 245—247° (Möhlau gives 217—218°). Its solution in alcohol is very pale yellow, and on the addition of alkali it becomes dark brown. The acid gives brown coloured salts with heavy metals:

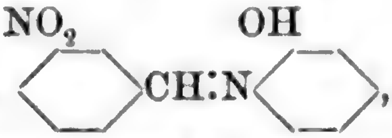
0·1952 gave 0·4193 CO_2 and 0·0654 H_2O. C = 58·58; H = 3·72.
$C_{14}H_{10}O_5N_2$ requires C = 58·74; H = 3·50 per cent.

m-*Nitrobenzylidene*-p-*aminophenol*,

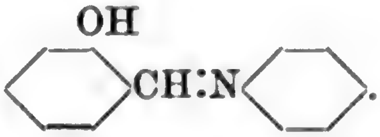


was prepared by mixing equivalent quantities of the components in warm dilute acetic acid. After some time the solution was poured into water, and precipitate crystallised, first from dilute acetic acid and finally from dilute alcohol. It separates in small, brown needles, which melt at 154°. Its alcoholic solution is pale yellow, and on the addition of alkali becomes slightly darker in shade:

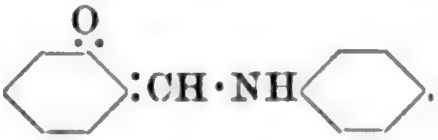
0·1992 gave 0·4673 CO_2 and 0·0763 H_2O. C = 63·98; H = 4·26.
$C_{13}H_{10}O_3N_2$ requires C = 64·46; H = 4·13 per cent.

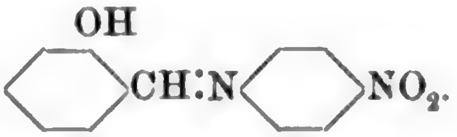
m-*Nitrobenzylidene-o-aminophenol*, , was obtained by condensing its components in absolute alcoholic solution. After a short time the solution was poured into water, and the precipitate crystallised from alcohol, from which it separated in fine, pale yellow, felted needles, melting at 135°. Its alcoholic solution is pale yellow, and on the addition of alkali becomes slightly darker in shade:

0·1874 gave 0·4378 CO_2 and 0·0729 H_2O. C = 63·71; H = 4·32.
$C_{13}H_{10}O_3N_2$ requires C = 64·46; H = 4·13 per cent.

o-*Hydroxybenzylideneaniline*, 

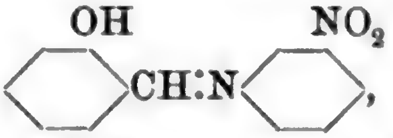
This compound has been prepared by Emmerich (*Annalen*, 1887, **241**, 344) and Duparc, *Annalen*, 1891, **266**, 140). It crystallises in pale yellow needles, and its alcoholic solution is pale yellow. On the addition of alkali to this no visible change was observed. Since the sodium salt of this compound shows less absorption than the free azomethine (see table), it might be suggested that the anhydro-compound in this case possesses a quinonoid structure and is to be formulated as



o-*Hydroxybenzylidene*-p-*nitroaniline*, 

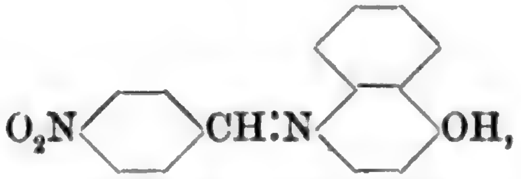
This compound has been previously prepared by Haarman (*Ber.*, 1873, **6**, 339), and is described as melting at 115°. By dissolving equimolecular quantities of salicylaldehyde and *p*-nitroaniline separately in dilute acetic acid, and mixing the solutions, a deep orange precipitate was obtained, which crystallised from dilute acetic acid in small needles melting at 159°. The preparation was repeated, and the same result was obtained, and a mixture of the two preparations also melted sharply at 159°. The substance dissolves in alcohol readily, and the dilute solution is pale yellow, but on the addition of alkali becomes reddish-brown in shade:

0·1636 gave 0·3843 CO_2 and 0·0634 H_2O. C = 64·07; H = 4·30.
$C_{13}H_{10}O_3N_2$ requires C = 64·46; H = 4·13 per cent.

o-*Hydroxybenzylidene*-m-*nitroaniline*, 

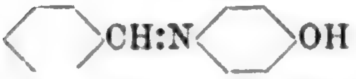
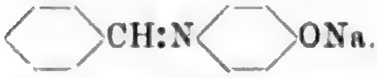
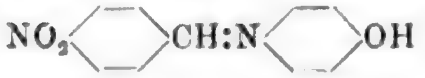
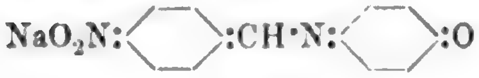
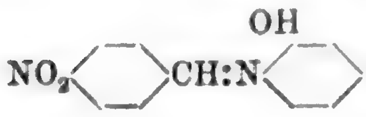
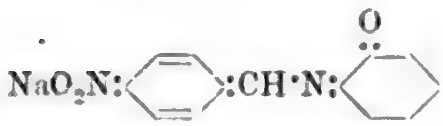
, was prepared by mixing equimolecular quantities of its components in dilute alcoholic solution. The resulting crystalline magma was filtered, and the substance recrystallised from absolute alcohol, from which it separated in pale yellow needles, melting at 132°. The alcoholic solution is pale yellow, and the solution remains practically unchanged on the addition of alkali:

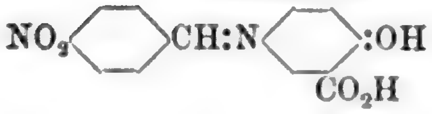
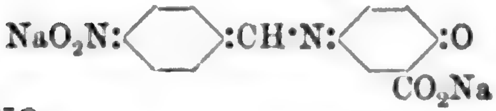
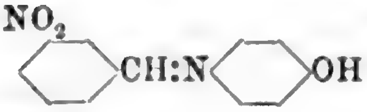
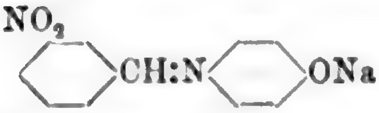
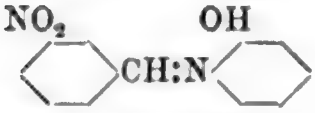
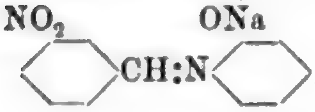
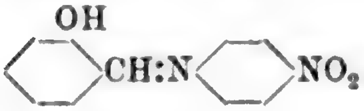
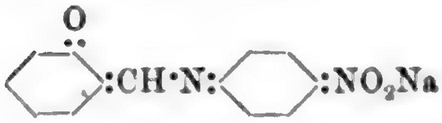
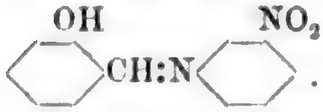
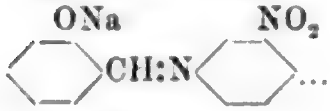
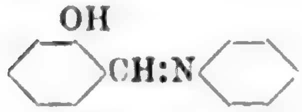
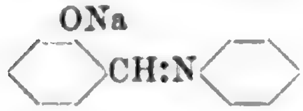
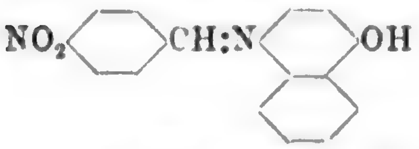
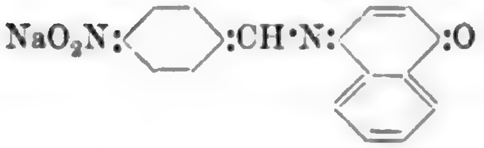
0·2020 gave 0·4794 CO_2 and 0·079 H_2O. C = 64·72; H = 4·35.
$C_{13}H_{10}O_3N_2$ requires C = 64·46; H = 4·13 per cent.

p-*Nitrobenzylidene*-4-*amino*-a-*naphthol*, 

, has been prepared by Möhlau (*loc. cit.*). It crystallises in red needles or plates and the alcoholic solution on the addition of alkali becomes violet.

So far as the spectroscopic observations are concerned, only the visible portion of the spectrum has been examined. The solutions examined were alcoholic, solutions of the sodium salts being prepared by adding a drop of 40 per cent. sodium hydroxide solution to the parent substance. The statement "From 528 μμ onwards," means that from 528 μμ onwards the blue and violet are absorbed as far as the visible spectrum extends.

Substance.	Concentration.	Absorption. (Red). (Violet).
..................	N/100	From 455 μμ onwards
..................	N/100	,, 473 μμ ,,
............	N/100	,, 482 μμ ,,
......	N/100	,, 622 μμ ,,
..................	N/100	,, 463 μμ ,,
.........	N/100	,, 533 μμ ,,

Substance.	Concentration.	Absorption. (Red). (Violet).
	*N*/1000	From 457 $\mu\mu$ onwards
	*N*/1000	,, 500 $\mu\mu$,,
	*N*/100	,, 453 $\mu\mu$,,
	*N*/100	,, 528 $\mu\mu$,,
	*N*/100	,, 455 $\mu\mu$,,
	*N*/100	,, 513 $\mu\mu$,,
	*N*/100	,, 463 $\mu\mu$,,
	*N*/100	,, 533 $\mu\mu$,,
	*N*/100	,, 465 $\mu\mu$,,
	*N*/100	,, 493 $\mu\mu$,,
	*N*/100	,, 482 $\mu\mu$,,
	*N*/100	,, 468 $\mu\mu$,,
	*N*/5000	,, 477 $\mu\mu$,,
	*N*/5000	Band 577 to 465 $\mu\mu$

I have to thank the Research Fund Committee for a grant which has partly defrayed the expense of this work.

EAST LONDON COLLEGE.

L.—*Some Physico-Chemical Properties of Mixtures of Pyridine and Water.*

By Harold Hartley, Noel Garrod Thomas, and
Malcolm Percival Applebey.

The behaviour of mixtures of pyridine and water has been studied from various points of view by a number of authors : Goldschmidt and Constam (*Ber.*, 1883, **16**, 2977) determined the composition of the constant boiling mixture ; Zawidzki (*Zeitsch. physikal. Chem.*, 1900, **35**, 129), the total and partial vapour-pressure curves at 80° ; Bredig (*Zeitsch. Elektrochem.*, 1901, **7**, 767), the absorption of electric waves ; Morgan and Kanolt (*J. Amer. Chem. Soc.*, 1906, **28**, 5721), the conductivity of solutions of silver nitrate in mixtures of the two liquids ; and, since the present work was begun, papers have appeared by Holmes (Trans., 1906, **90**, 1784) on the densities of mixtures at 15°, and by Dunstan, Thole, and Hunt (Trans., 1907, **91**, 1718) on the density and viscosity at 25°. The consideration of the two facts, that both liquids dissolve metallic salts, forming conducting solutions, and that the properties of mixtures of the two liquids differ largely from the properties of their constituents, led us to undertake the determination of those properties of the mixtures which affect the electrical conductivity of salts dissolved in them in the hope that the gradual substitution of one solvent for the other might throw some further light on the causes determining the conductivity of solutions.

The determination of the following constants is described in the present paper : the density, viscosity, and surface tension of pyridine-water mixtures at 0° and 25° ; the density and viscosity of one-eighth weight-normal solutions of lithium nitrate in a series of mixtures at 0° and 25°, and the molecular conductivity of these solutions at the same temperatures. With the help of these data, we have attempted to trace how far the observed changes in conductivity are due to (1) the extent of ionisation, (2) the viscosity of the solution, and (3) the condensation of solvent round the ions.

Lithium nitrate was selected because it dissolved freely in both liquids and in mixtures of them ; preliminary experiments with salts of lithium, potassium, and sodium showed that only those salts of these metals which are hygroscopic dissolve easily in pyridine.

Preparation of Materials.

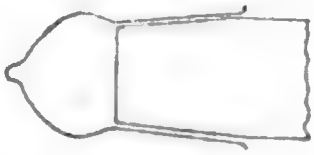
The best pyridine obtained from Kahlbaum was found to contain traces of water, from which it could be freed only by repeated treatment with solid potash and distillation with a fractionating column.

The great difficulty of drying the substance is probably due to the formation of a compound with water. The dry substance is extremely hygroscopic, and it was always distilled directly into a dry bottle protected from moisture by a calcium chloride tube. The substance used in our experiments boiled at 115·3—115·4° (corr.); Zawidzki (*Chem. Zeit.*, 1906, **30**, 299) found 115·1—115·3°, and Innes (Trans., 1901, **79**, 261), 115·2—115·5°. If contaminated with small traces of water, the boiling point is several tenths of a degree lower. The pyridine was kept in desiccators in the dark.

Water.—This was purified by distillation with acid and alkaline permanganate in the manner described by Manley (*Proc. Roy. Soc.*, 1905, **76**, *A*, 476), a block-tin condenser being used for the final condensation. Its conductivity was on an average $1{\cdot}2 \times 10^{-6}$ reciprocal ohms at 0°. The water was stored in litre flasks of Jena glass, in which it kept unaltered for several weeks. The flasks had caps ground on to the outside surface instead of the ordinary inside stopper, as shown in Fig. 1.

This ensures the water being poured out over a clean surface, and avoids the danger of dirt dropping in when the flask is opened. The device makes it easier to keep and use conductivity water without risk of contamination, and is of great convenience in dealing with dilute solutions.

FIG. 1.



Lithium Nitrate.—Obtained from Kahlbaum, and further purified by recrystallisation. The spectrum of the recrystallised salt showed no traces of the lines of any impurities except a faint sodium line.

Preparation of Solutions.—All the solutions were made up by weight, and kept in Jena glass flasks with ground stoppers. As lithium nitrate is very hygroscopic, the following method was adopted for making up the salt solutions. About the right weight of the hydrated salt was dehydrated by heating it in a small platinum crucible in an air-bath at 175° for at least six hours; the crucible was allowed to cool in a desiccator, and weighed as soon as cool in a stoppered glass bottle, the weight of the bottle and crucible being previously ascertained. The correct weight of solvent required was then weighed into a wide-mouthed stoppered bottle, and the crucible was dropped in. The composition of the solution by weight was thus accurately known, and, in order to find the number of gram-equivalents of salt in a litre of solution, density determinations were made at the temperature at which the solution was used.

Thermostats.—For experiments at 25°, a large thermostat with glass front, holding about 40 litres, provided with a spiral temperature regulator (Lowry, Trans., 1905, **87**, 1039), gave excellent results; the temperature variation rarely exceeded ±0·01°; the actual corrected temperature was 25·08° on the hydrogen scale. For experiments at 0°, a bath containing finely-powdered ice was used, and, for the conductivity determinations, this was jacketed by a second vessel containing ice. The temperature never exceeded +0·05°, and was usually much closer to 0°. The thermometers used were graduated in wide twentieths of a degree, and were compared with a thermometer with a Reichsanstalt certificate.

Density Determinations.

The determinations at 25° were made in two U-shaped pyknometers of a pattern recommended to us by Mr. J. J. Manley. They were made from test-tube glass, and held about 9 c.c. Each pyknometer was weighed against a counterpoise, and the results were corrected for displaced air. Considering the small quantities used, the results show good agreement except near the pyridine end of the series. Pyridine is so hygroscopic that it absorbs sufficient water during the filling of a pyknometer to affect its density appreciably. In one case, an exposure to the air of about five minutes caused the density to rise by 3 units in the fourth place.

The results are given in the following table, and are plotted in Fig. 2:

Table I.—*Density of Pyridine-Water Mixtures at* 25·08°.

Percentage of pyridine.	Molecular percentage of pyridine.	Δ_4^{25} by pyknometer I.	Δ_4^{25} by pyknometer II.	Δ_4^{25}, mean value.
0·00	0·00	—	—	0·99705
9·91	2·45	0·99953	0·99953	0·99953
19·28	5·16	1·00118	1·00116	1·00117
29·99	8·90	1·00231	1·00236	1·00234
39·84	13·12	1·00313	1·00314	1·00314
49·57	18·31	1·00345	1·00349	1·00347
59·70	25·22	1·00295	1·00298	1·00297
70·34	35·09	1·00127	1·00125	1·00126
80·15	47·92	0·99686	0·99702	0·99694
90·08	67·44	0·98864	0·98877	0·98870
95·01	81·26	0·98311	—	0·98311
100·00	100·00	0·97710	0·97732	0·97721

Zawidzki gives two results for the density at 25°, namely, 0·97794 and 0·97796; it would thus seem as if his specimen had absorbed a little water.

On account of the large expansion with rise of temperature of mixtures containing a large proportion of pyridine, the pyknometers used for the determinations at 0° were made of tube form and stoppered. The results were not so accurate as those at 25°, but duplicate determinations rarely differed by more than 1 unit in the fourth place.

The results are given in the following table, and are plotted in Fig. 2:

TABLE II.—*Density of Pyridine-Water Mixtures at* 0°.

Percentage of pyridine.	Molecular percentage of pyridine.	Δ_4^0 by pyknometer I.	Δ_4^0 by pyknometer II.	Δ_4^0, mean value.
0·00	0·00	—	—	0·99987
9·59	2·36	1·00571	1·00583	1·00577
20·50	5·64	1·01161	1·01155	1·01158
29·53	8·72	1·01509	1·01517	1·01513
39·73	13·06	1·01860	1·01856	1·01858
49·84	18·47	1·02160	1·02166	1·02163
59·16	24·83	1·02310	1·02324	1·02317
62·02	27·13	1·02342	1·02362	1·02352
65·12	29·85	1·02354	1·02364	1·02359
69·92	34·62	1·02343	—	1·02343
87·07	47·80	1·01967	1·01967	1·01967
90·07	67·46	1·01190	1·01191	1·01191
100·00	100·00	1·00120	1·00134	1·00127

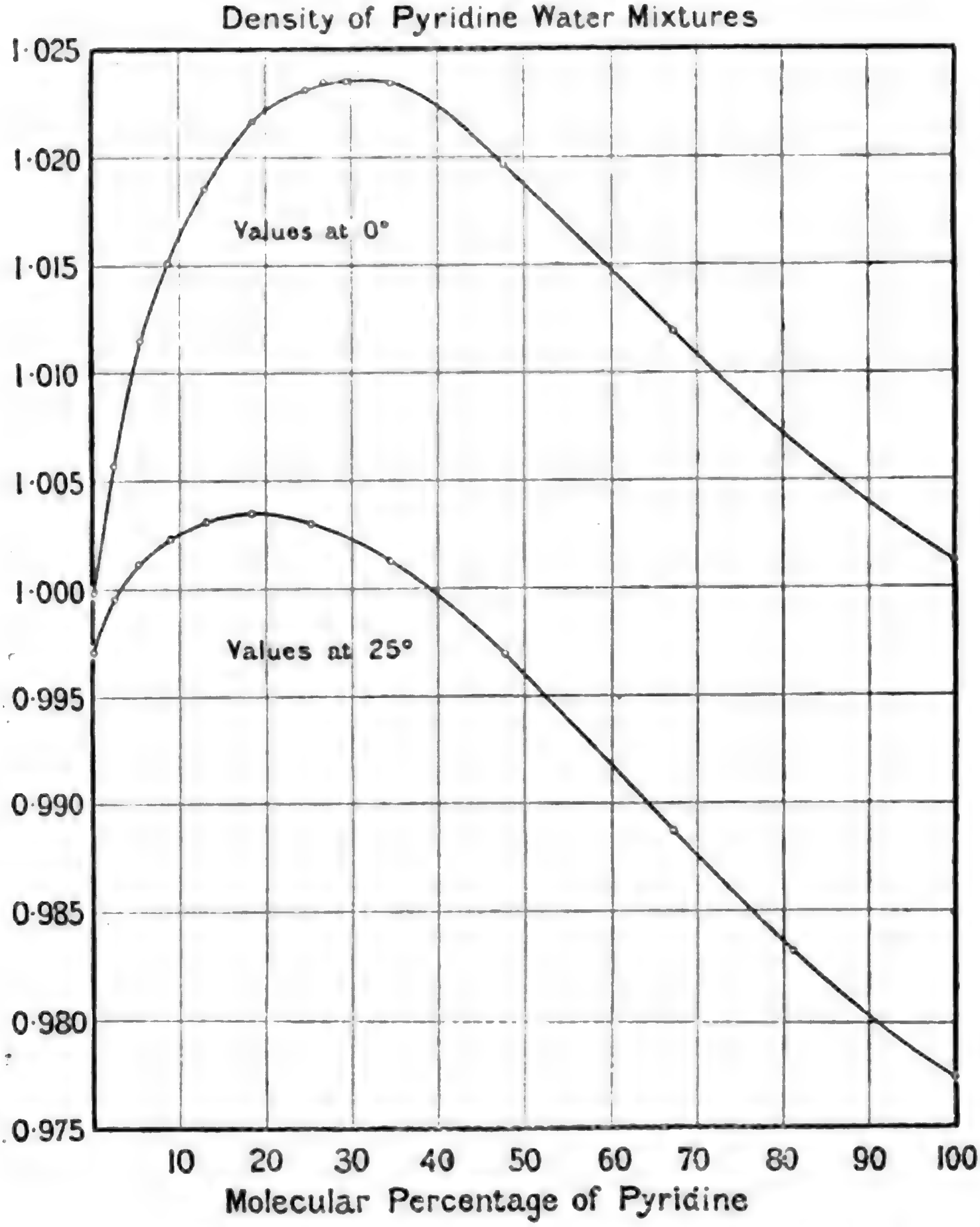
Both curves show a maximum, which occurs at 31 molecules per cent. of pyridine at 0°, and at 18 molecules per cent. at 25°. The shift in the maximum is easily explained by the difference in the coefficients of expansion of water and pyridine between 0° and 25°, pyridine expanding almost twenty times as much as water. The large amount of contraction which takes place when the two liquids are mixed, and also the considerable heat evolution accompanying it, point to the formation of a hydrate of pyridine in the mixture, and, as in both curves the maximum deviation from the straight line joining the two ends of the curve occurs at 30 molecules per cent. of pyridine, the maximum formation of hydrate probably takes place in mixtures of this composition. This result is confirmed by the viscosity curves, which show similar maxima at 29 molecules per cent. of pyridine at 0°, and 30·5 molecules per cent. at 25°.

In a recent paper (*loc. cit.*), Dunstan, Thole, and Hunt describe a series of determinations of the density of pyridine–water mixtures at 25°, in which they find discontinuities in the density-concentration curve at 36 and 62 per cent. of pyridine. We found no evidence of the existence of these discontinuities either at 25° or at 0°, and, if the results given in the above paper are plotted against ours, it is evident that the supposed breaks in the curve are due to the authors' practice of drawing curves through their experimental points without taking into account their probable experimental error.

But apart from experimental evidence, other considerations make it improbable that the curves given by the above authors represent real phenomena.

Any continuous change in the composition of a homogeneous mixture must be accompanied by a continuous change in physical properties, as a discontinuity could only be produced by some abrupt change in the equilibrium constant of one of the systems present, and any change of this nature would be contrary to the law of mass action.

FIG. 2.



If we accept the law of mass action, no homogeneous liquid mixture can show a discontinuous change of density with composition while its temperature and pressure remain constant.

Density of ⅛ Weight-normal Solutions of Lithium Nitrate in Pyridine–Water Mixtures.

Determinations of the density of ⅛ weight-normal lithium nitrate solutions at 0° and 25° were needed in order to calculate their normality and for the viscosity experiments. The determinations were made either in bottle pyknometers holding 10 c.c. with a glass cap ground to fit over the stopper, or in pyknometers of the form used for the mixture at 0°. Duplicate determinations were not made, as the density was only required to the nearest unit in the third decimal place. The results are given in the following table:

TABLE III.—*Density of ⅛ Weight-normal Solutions of Lithium Nitrate in Pyridine–Water Mixtures at* 0° *and* 25·08°.

Percentage of pyridine in solvent.	Molecular percentage of pyridine.	Δ^{0}_{4} of solution.	Δ^{25}_{4} of solution.
0·00	0·00	1·0055	1·0020
21·61	5·91	1·0170	1·0062
42·61	14·47	1·0240	1·0075
67·38	31·28	1·0285	1·0074
75·09	40·64	1·0276	1·0051
79·34	46·67	1·0259	1·0035
83·93	54·35	1·0225	1·0003
88·53	63·77	1·0189	0·9965
92·50	73·76	1·0156	0·9920
95·01	81·27	—	0·9897
97·46	89·75	1·0107	—
100·00	100·00	1·0085	0·9840

Viscosity of Pyridine–Water Mixtures.

The viscosity of pyridine–water mixtures was compared with that of water at 0° and 25° by means of viscometers of the Ostwald pattern. The times taken by equal volumes of mixture and of water to flow through the capillary were measured by a stop-watch reading to ⅕ sec., and, from the times of flow and the densities, the relative viscosity was calculated by the formula:

$$\text{relative viscosity of mixture} = \frac{\text{time for mixture}}{\text{time for water}} \times \frac{\text{density of mixture}}{\text{density of water}}.$$

An example is given of a set of determinations with a mixture containing 18·47 molecules per cent. of pyridine at 0°:

Mean time of flow in viscometer with water = 103·6 secs.

	1st filling.	2nd filling.
Times of flow with mixture, in secs.	290·8	291·2
	291·2	291·3
	291·0	291·2
	291·0	291·0

Mean = 291·1 secs.

Density of mixture = 1·0126.

$$\text{Viscosity relative to water} = \frac{291{\cdot}1}{103{\cdot}6} \times \frac{1{\cdot}0216}{0{\cdot}9998} = 2{\cdot}894.$$

In calculating the viscosity in absolute units, Thorpe and Rodger's values for water at 0° and 25·08° were used, namely, 0·01778 and 0·00890. Four sets of determinations were usually made with each mixture (two sets in each tube), and the results usually agreed to 0·3 per cent. The most frequent cause of difficulty was specks of dust and traces of grease in the capillary; after a small number of trials with different liquids, including freshly-distilled alcohol and ether, we found that the safest method of cleaning the tubes was to place in them some fuming nitric acid and to add some alcohol, and then, after rinsing them with the best conductivity water, they were dried in a small air-bath by means of a current of dust-free air. The results became more concordant after this method of treatment had been adopted.

As many of the mixtures are hygroscopic, calcium chloride tubes were attached to both arms of the viscometer, for without this precaution the mixtures rich in pyridine absorbed water during an experiment. The tubes were always set in a vertical position with a plumb line. The results are given in the following tables and plotted on the lower line in Figs. 3 and 4:

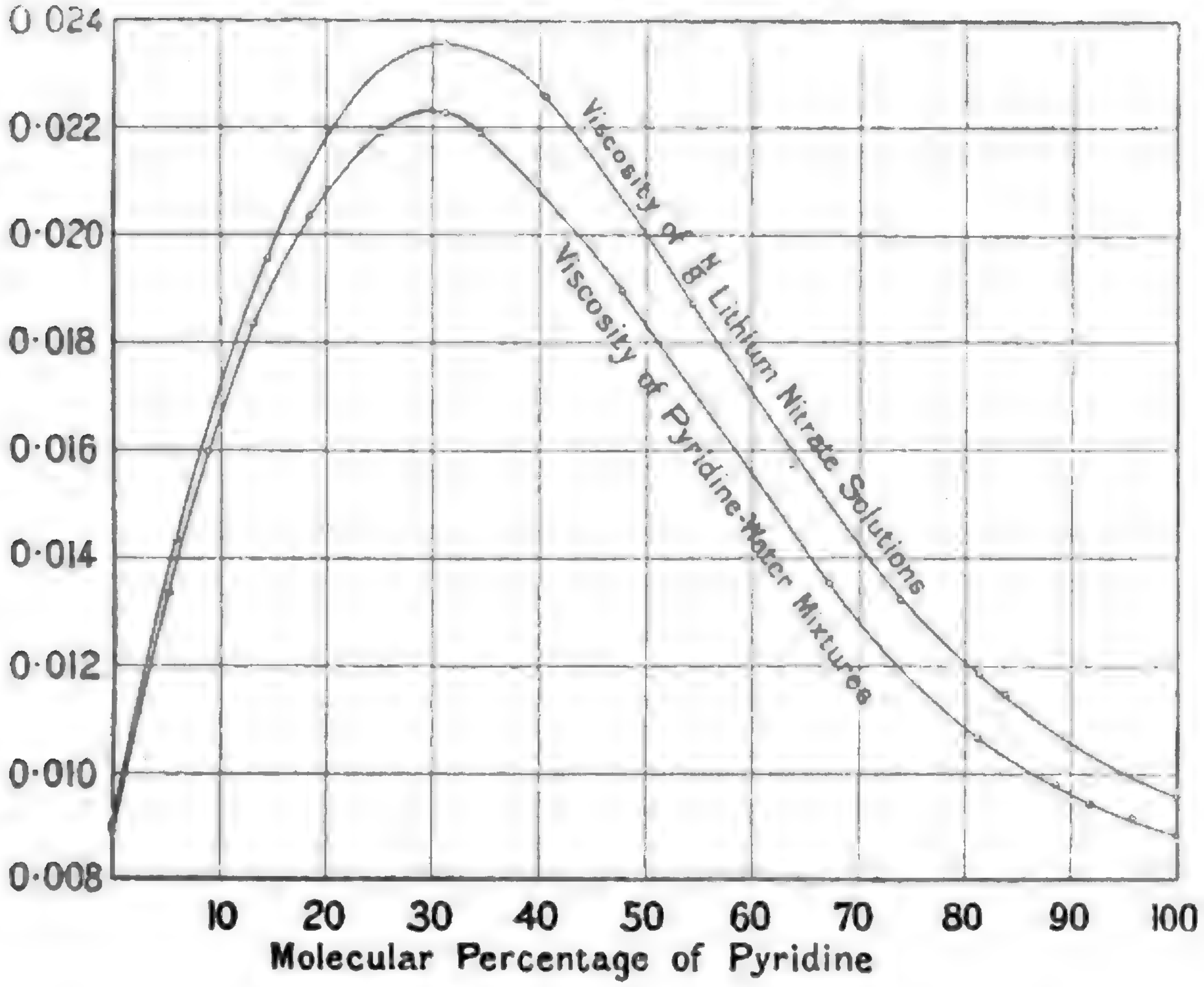
TABLE IV.—*Viscosity of Pyridine–Water Mixtures at* 25·08°.

Percentage of pyridine in mixture.	Molecular percentage of pyridine.	Viscosity relative to water by viscometer I.	Viscosity relative to water by viscometer II.	Mean value of viscosity in absolute units.
0·00	0·00	1·000	1·000	0·00890
9·91	2·40	1·255	1·253	0·01116
19·28	5·15	1·503	1·499	0·01336
29·99	8·90	1·797	1·794	0·01598
39·84	13·12	2·062	2·060	0·01833
49·57	18·40	2·289	2·279	0·02032
59·70	25·22	2·462	2·454	0·02187
66·65	31·27	2·500	—	0·02225
70·34	34·50	2·460	2·454	0·02186
80·15	47·80	2·130	2·129	0·01894
90·08	67·30	1·521	1·513	0·01350
95·01	81·26	1·194	1·200	0·01064
97·16	88·64	1·100	—	0·00979
98·02	91·86	1·058	—	0·00942
99·00	95·76	1·030	—	0·00917
100·00	100·00	0·9943	0·9945	0·00885

TABLE V.—*Viscosity of Pyridine-Water Mixtures at 0°.*

Percentage of pyridine.	Molecular percentage of pyridine.	Viscosity relative to water by viscometer I.	Viscosity relative to water by viscometer II.	Mean viscosity in absolute units.
0·00	0·00	—	—	0·01778
9·59	2·36	1·374	1·378	0·02447
20·50	5·64	1·807	1·813	0·03218
29·53	8·72	2·157	2·163	0·03840
39·73	13·06	2·558	2·562	0·04548
49·84	18·47	2·894	2·897	0·05147
59·16	24·83	3·102	3·109	0·05521
62·02	27·13	3·126	3·131	0·05562
65·12	29·85	3·125	3·129	0·05560
69·92	34·62	3·044	3·048	0·05416
75·75	41·59	2·758	2·759	0·04905
80·07	47·80	2·392	2·402	0·04262
85·13	57·89	1·853	1·857	0·03298
90·07	67·46	1·346	1·351	0·02398
95·11	81·59	0·9714	0·9736	0·01729
97·84	91·17	0·8210	0·8248	0·01463
100·00	100·00	0·7394	0·7468	0·01321

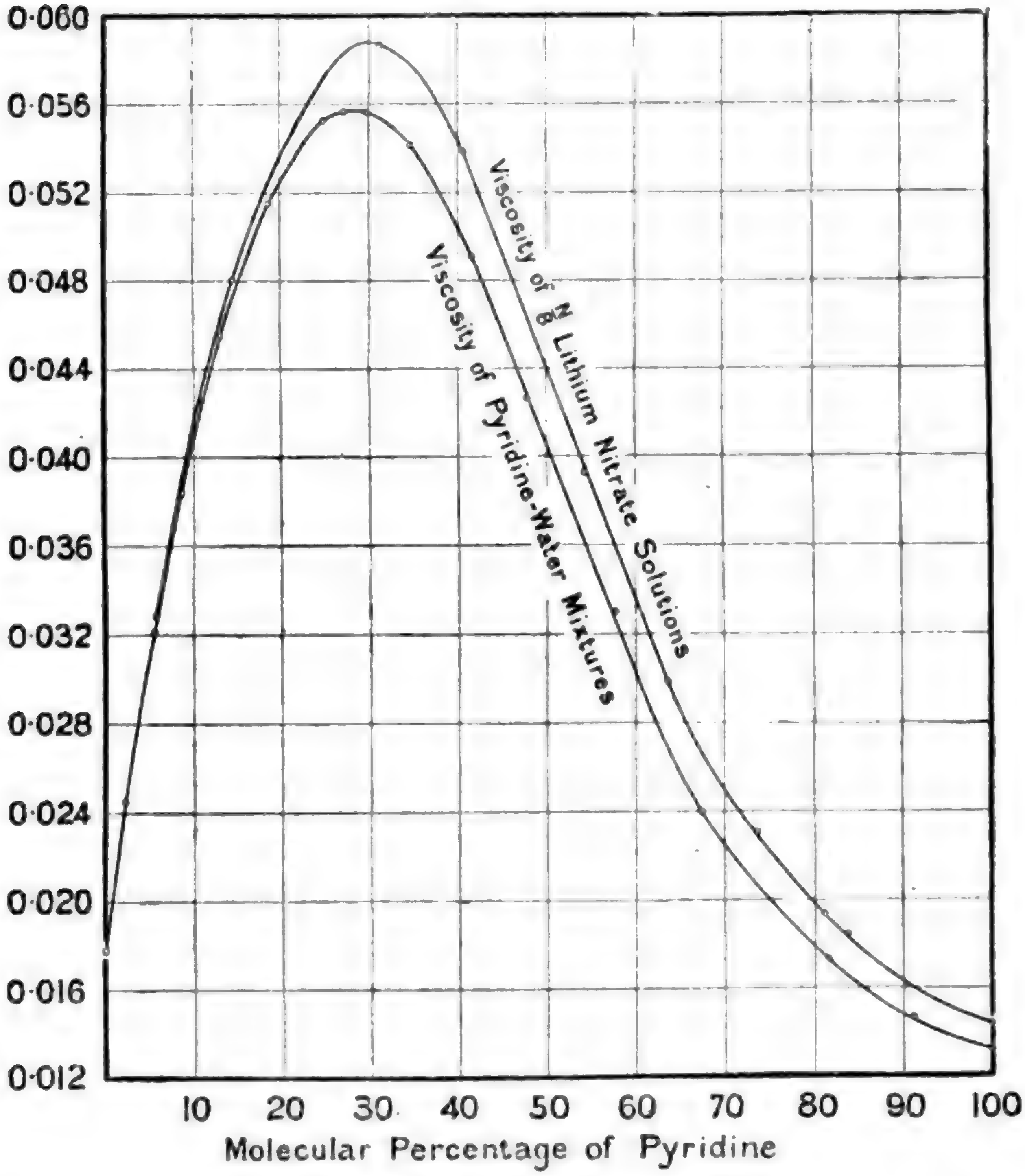
FIG. 3.



The experimental values, when plotted, lie on fairly smooth curves, which show a maximum in both cases and a point of inflexion between the maximum and pyridine end. We did not observe any of the discontinuities mentioned by Dunstan, Thole, and Hunt (*loc. cit.*), and a comparison of their curve with ours leaves no doubt that, as in the case of density determinations, these are due to no allowance being made for experimental error.

At 0°, the maximum occurs at 28·5 molecules per cent. of pyridine, and at 25° at 30·5 molecules per cent. of pyridine, the maximum deviation from the straight line joining the end values occurs at

FIG. 4.



29 molecules per cent. and at 30·5 molecules per cent. of pyridine, at 0° and 25° respectively.

Thus the viscosity values support the deduction from the density curves, that the maximum amount of hydration of the pyridine takes place in the neighbourhood of 30 molecules per cent. at both temperatures.

Viscosity of $\frac{1}{8}$ Weight-normal Lithium Nitrate Solutions.

With the lithium nitrate solutions, two sets of determinations were made at each temperature, and the results are given in the following table and are plotted on the upper line in Figs. 3 and 4 :

TABLE VI.—*Viscosity of $\frac{1}{8}$ Weight-normal Solutions of Lithium Nitrate in Pyridine–Water Mixtures at* 0° *and* 25·08°.

Percentage of pyridine in solvent.	Molecular percentage of pyridine.	Viscosity of solution relative to water at 0°.	Viscosity of solution in absolute units at 0°.	Viscosity of solution relative to water at 25°.	Viscosity of solution in absolute units at 25°.
0·00	0·00	1·004	0·01785	1·014	0·00903
21·61	5·91	1·848	0·03286	1·609	0·01433
42·61	14·47	2·700	0·04801	2·206	0·01964
67·38	31·28	3·298	0·05865	2·648	0·02356
75·09	40·60	3·028	0·05383	2·533	0·02254
83·93	54·35	2·208	0·03925	2·100	0·01869
88·53	63·77	1·677	0·02982	1·768	0·01573
92·50	73·76	1·296	0·02305	1·485	0·01321
95·01	81·27	1·089	0·01936	1·329	0·01183
95·83	83·98	1·037	0·01843	1·288	0·01146
100·00	100·00	0·810	0·01439	1·075	0·00957

It will be seen that as the composition of the solvent varies, the addition of 0·125 gram-molecule of salt has a very different effect on its viscosity. At 25°, the increase is only 1·5 per cent. in water, but the change becomes gradually larger in the mixture until it reaches a maximum of 9·4 per cent. in the 75 per cent. mixture. From this point, it falls slightly to 8·27 per cent. in pure pyridine. At 0°, the changes are of about the same order of magnitude.

The general result of investigations on the viscosity of liquids has been to show that a liquid becomes more viscous when the average bulk of the particles of which it is composed is increased; the behaviour of water at different temperatures and pressures is a striking instance of this (Röntgen, *Wied. Ann.*, 1884, [iii], **22**, 510, and 1892, [iii], **45**, 91 ; R. Cohen, *Wied. Ann.*, 1892, [iii], **45**, 666).

The changes in our experiments might be ascribed to (1) the disturbance of the equilibrium existing between the constituents of the solvent; (2) the introduction of molecules and ions of solute, and (3) the aggregation of particles of solvent round these.

The curve giving the relations between ionisation and composition of solvent in *N*/8 solutions on p. 546 shows that in pyridine the salt is very slightly dissociated (not more than 2 per cent.), so that the increase of viscosity at the end of the curve must be due to the condensation of pyridine round the lithium nitrate molecules. In all mixtures up to 60 molecules per cent. of pyridine, most of the salt is ionised, and the increase of viscosity must therefore be caused mainly by the condensation of solvent round the ions. The form of the curve indicates that this condensation is greater in the pyridine–water mixtures than in water, and this conclusion is strongly supported by the evidence based on the electrical conductivity at infinite dilution (see p. 550).

Surface Tension of Pyridine–Water Mixtures.

The surface tension of the mixtures was determined by Jaeger's method, in which the minimum pressure required to drive a stream of air bubbles from a capillary opening immersed in a liquid is measured. In this way, the surface is constantly renewed, and irregularities due to changes in the surface layer are avoided. An apparatus was constructed on the same lines as that described by Whatmough (*Zeitsch. physikal. Chem.*, 1901, **39**, 129), and the precautions mentioned by him were carefully observed. Very fine capillary tubes were drawn and cut off so that the capillary did not exceed 2 mm. in length; they were put just below the surface of freshly-distilled water contained in a boiling tube standing in a thermostat; the minimum pressure necessary to maintain a stream of air bubbles was measured by means of a sulphuric acid manometer 3 metres high. A similar measurement was then made with a second liquid, and the ratio of the two pressures gave the ratio of the surface tensions. For pure liquids, the method seemed to give very definite results; the following is a comparison of the values for pyridine with those of Ramsay and Shields (Trans., 1893, **63**, 1089):

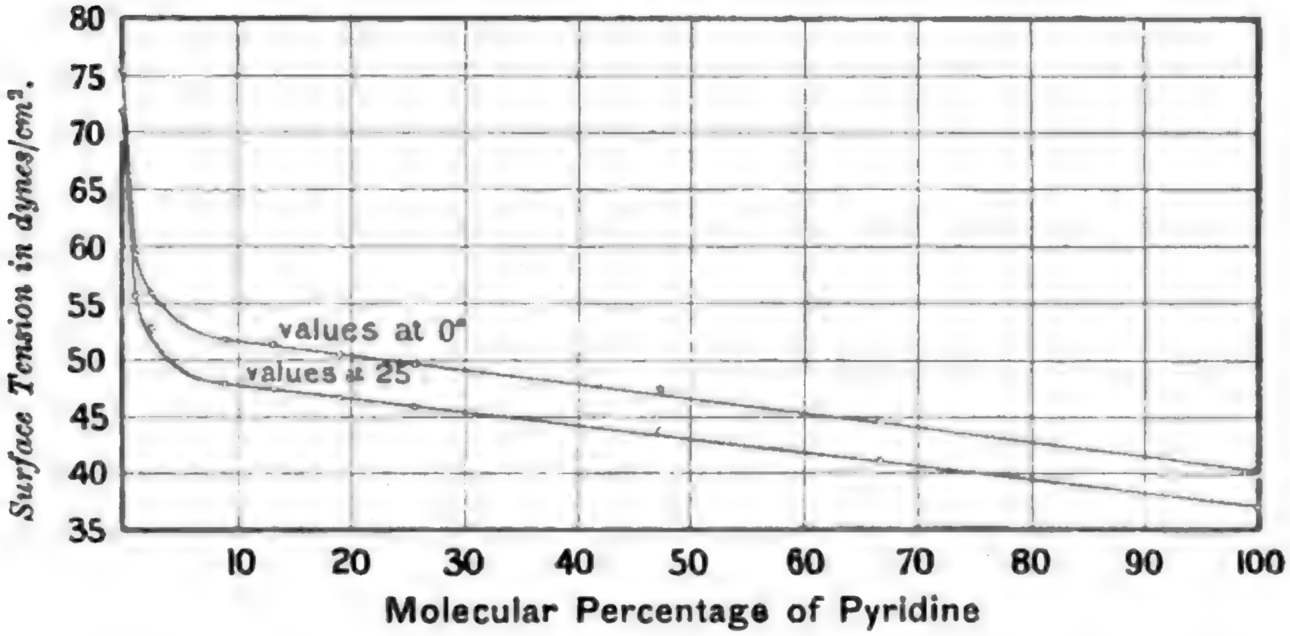
Temp.	γ by tube 1.	γ by tube 2.	Mean value in dynes/cm^2.	Interpolated value.	Ramsay and Shields.
0·0°	39·94	40·33	40·1	—	—
17·12	—	—	—	38·1	38·40
25·00	37·04	36·96	37·0	—	—
46·20	—	—	—	33·8	34·17
50·00	33·05	33·34	33·2	—	—

The difference between the two sets of values may be explained by the fact that our values give γ for pyridine in contact with air, whilst in Ramsay and Shields' experiments it was in contact with saturated pyridine vapour. The mixtures were more troublesome, as the fine capillaries soon ceased to give trustworthy values. The results are given in the following table and curve:

TABLE VII.—*Surface Tension of Pyridine-Water Mixtures at 0° and 25°.*

		Values at 0°.			Values at 25°.		
Percentage of pyridine.	Molecular percentage of pyridine.	Surface tension by tube I.	Surface tension by tube II.	Mean value in dynes/cm².	Surface tension by tube I.	Surface tension by tube II.	Mean value in dynes/cm²
0	0	—	—	75·49	—	—	71·78
4·92	1·06	59·3	—	59·3	55·6	—	55·6
10·20	2·52	55·9	—	55·9	52·8	—	52·8
30·22	8·98	51·75	51·85	51·8	47·85	47·90	47·9
40·00	13·19	51·4	51·2	51·3	47·3	47·5	47·4
49·27	19·00	50·2	50·7	50·5	46·3	47·0	46·6
60·16	25·60	49·4	49·8	49·6	45·6	46·0	45·8
79·73	47·28	47·4	—	47·4	43·7	—	43·7
89·80	66·69	44·5	—	44·5	41·0	—	41·0
100·00	100·00	40·35	39·95	40·15	36·95	37·05	37·0

FIG. 5.



In dilute solutions of pyridine, foam is readily formed and persists for some time; in stronger solutions this tendency disappears.

Marangoni (*Nuovo Cim.*, 1871–2, **5–6**, 239) and Rayleigh (*Proc. Roy. Soc.*, 1889, **47**, 281) have pointed out that the stability of a film of solution probably depends on a difference in concentration between the surface and the interior of the liquid. Milner, in a recent paper (*Phil. Mag.*, 1907, [vi] **13**, 96), shows that the "surface excess," that is, the number of gram-molecules of the solute which are drawn out from the interior in the formation of each sq. cm. of the surface, may be calculated by means of the equation:

$$\sigma = \frac{1}{iRT}\frac{d\tau}{d\log_e c},$$

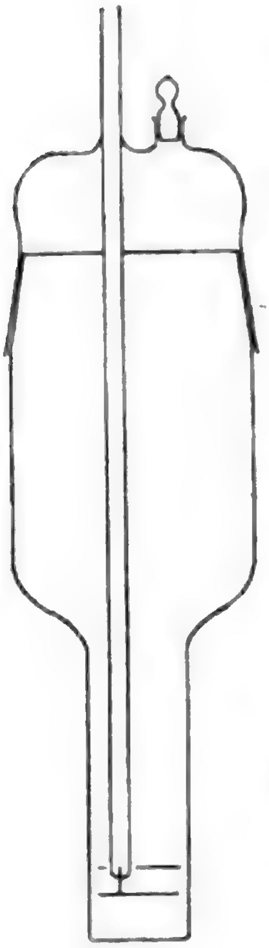
where τ is the surface tension, c the concentration, i the coefficient of ionisation, R the constant of the gas equation, and σ the surface excess.

Thus, if the surface tension varies linearly with the logarithm of the concentration, the surface excess will be constant. This condition is fulfilled approximately by dilute solutions of pyridine in water, and the surface excess is calculated to be 2×10^{-6} gram-molecule per sq. cm., or 0·16 milligram per sq. metre.

For acetic acid dissolved in water, Milner found an excess of $3{\cdot}3 \times 10^{-6}$ gram-molecule per sq. cm., or 0·2 milligram per sq. metre, and for sodium chloride a surface deficit (since the surface tension increases with concentration) of $4{\cdot}09 \times 10^{-6}$ gram-molecule per sq. cm., or 0·024 milligram per sq. metre.

If we take the thickness of the surface layer as being of the order of 50×10^{-6} mm. (Rücker, Trans., 1888, **53**, 222), the excess concentration of pyridine in the surface layer is 3·2 milligrams per c.c.

FIG 6.



Electrical Conductivity of Lithium Nitrate dissolved in Pyridine-Water Mixtures.

The conductivity of solutions of lithium nitrate in the various mixtures was determined at 0° and at 25° by the ordinary telephone method. In each experiment, a one-eighth weight-normal solution was made up in the manner described on page 539, 20 c.c. of this solution were then introduced into the conductivity cell, and successive dilutions were performed by means of two accurately calibrated 10 c.c. pipettes. The solvent was always kept in the same bath as the solution, and the dilution was carried on in all cases to $v = 1024$, and in a few to $v = 4096$.

As the conductivity of the solvent changed quickly on exposure to air, owing to the absorption of carbon dioxide, a conductivity cell of the form shown in the accompanying diagram was used.

It was found very convenient to have the lid ground on outside the cell. The cells were made of borosilicate glass by Mr. Baumbach, glass blower to the University of Manchester, who also made most of the glass apparatus used in the work.

The electrodes, after being coated with platinum black, were heated in a blowpipe flame as recommended by Whetham (*Phil. Trans.*, 1900, *A*, **194**, 321), in order to avoid the possible absorption of the solute by the finely-divided metal. A Köhler bridge, coil, and telephone were used, and a dial resistance box made by Paul, which had been compared with a set of standard resistances by Edlmann.

Three separate readings were made for each resistance, and they usually agreed to 1 part in 1000. The conductivity of the solvent was determined at intervals during the dilutions, and the value found was subtracted from that of the solution.

The molecular conductivity was then calculated with the help of the density determinations for the original solution, neglecting the change of volume which takes place during successive dilutions. The error thus introduced falls within the experimental error for solutions between *N*/8 and *N*/1024. The constants of the cells used at 0° and 25° respectively were determined frequently during the progress of the experiments by means of *N*/50 potassium chloride solutions made up with freshly-distilled conductivity water. An example of a calculation is given to make the procedure quite clear:—Solution of lithium nitrate in 5·91 molecules per cent. pyridine–water mixture; solution made up by weight to contain 1 gram-molecule of lithium nitrate in 8000 grams of solution; the density of solution at 25·08° was found to be 1·0062.

The determination of the conductivity of the original solution at 25·08° gave the following results:

Resistance in box, in ohms.	Bridge reading.	Bridge reading corrected.	Resistance of cell.	Mean resistance.
57	50·25	50·05	57·21	—
58	49·80	46·60	57·08	57·11
56	50·70	50·50	57·18	—

Resistance of cell and leads	57·11
Correction for leads	0·04
	57·07

Specific conductivity of solutions calculated by cell constant ...	0·007303
Correction for solvent conductivity	0·000008
	0·007295

Molecular conductivity = 58·00 ; $m^{\frac{1}{2}} = 0·5010$.

The molecular conductivities at various dilutions were then plotted against $m^{\frac{1}{2}}$ (m being the concentration of solute in gram-molecules per litre), and from these curves the values for the molecular conductivity at dilutions 8, 16, 32, &c., were read off and the values for infinite dilutions found by extrapolation. The curves for solutions of lithium nitrate in water and in 31·28 per cent. mixture, both at 25·08°, are given in Fig. 7 as specimens.

The dotted vertical lines represent the values of $m^{\frac{1}{2}}$ corresponding with $v = 8$, 16, &c.

The results of the conductivity determinations are collected in the following tables, and curves for $v = \infty$, 1024, 256, 64, and 8 at 25·08° and 0° are shown in Figs. 8 and 9 on pp. 554, 555.

FIG. 7.

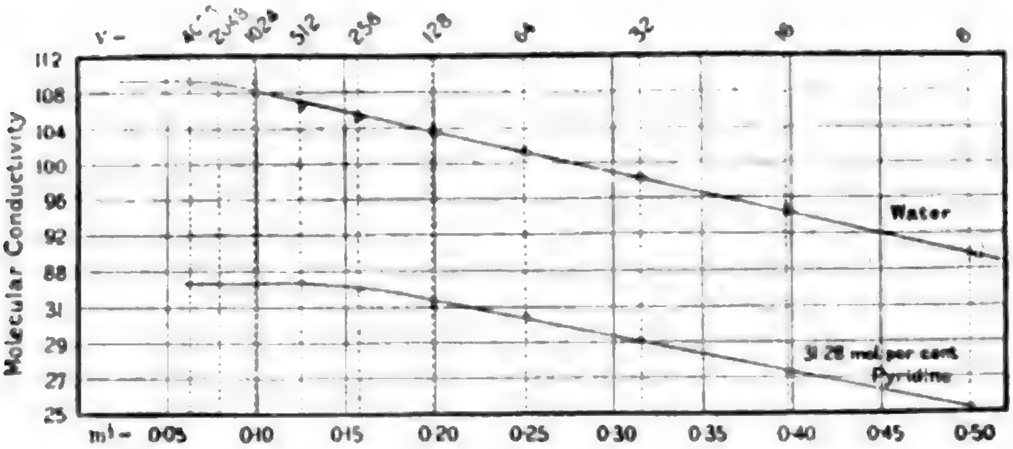


TABLE VIII.—*Molecular Conductivity of Lithium Nitrate Solutions in Pyridine-Water Mixtures at 25·08°.*

Molecular percentage of pyridine in solvent.	Molecular conductivity at various dilutions.								
	$V = \infty$.	1024.	512.	256.	128.	64.	32.	16.	8.
0·00	109·4	108·3	107·1	105·6	103·7	101·3	98·3	94·5	89·7
5·91	68·5	68·4	68·17	67·6	66·45	65·05	63·25	60·95	58·05
14·47	47·5	47·40	47·20	46·85	46·15	44·90	43·50	41·75	39·40
31·28	32·4	32·4	32·4	32·1	31·4	30·4	29·05	27·35	25·20
40·64	31·8	31·6	31·55	31·15	30·10	28·75	27·15	25·10	22·60
46·67	32·0	31·9	31·7	31·2	30·0	28·4	26·6	24·35	21·50
54·35	33·9	33·5	32·8	31·8	30·5	28·6	26·4	24·2	21·2
63·77	37·5	35·8	35·4	34·0	31·9	29·6	27·1	23·9	20·0
73·76	46·0	41·6	39·6	37·0	33·8	30·3	26·8	22·9	19·1
81·27	54·0	42·7	39·7	36·7	32·7	28·6	24·6	20·8	16·7
83·98	60·0	44·2	40·4	36·2	31·9	27·5	23·3	19·3	15·8
89·75	75·0	42·9	37·8	32·3	27·1	22·8	18·8	14·9	11·7

TABLE IX.—*Molecular Conductivity of Lithium Nitrate Solutions in Pyridine-Water Mixtures at 0°.*

Molecular percentage of pyridine in solvent.	Molecular conductivity at various dilutions.								
	$V = \infty$.	1024.	512.	256.	128.	64.	32.	16.	8.
0·00	57·10	56·95	56·55	55·75	54·80	53·65	52·20	50·25	48·15
5·91	29·85	29·85	29·75	29·63	29·35	28·92	28·30	27·64	26·75
14·47	19·05	19·05	19·05	19·05	18·86	18·66	18·30	17·77	17·10
31·28	13·25	13·25	13·25	13·15	12·95	12·60	12·18	11·60	10·80
40·64	13·40	13·36	13·30	13·20	12·95	12·50	11·85	11·05	10·00
46·67	—	—	—	—	—	12·85	12·10	11·25	10·20
54·35	16·25	16·10	16·05	15·85	15·25	14·30	13·25	12·10	10·75
63·77	21·2	20·5	20·0	19·07	17·95	16·70	15·35	13·75	11·80
73·76	27·5	24·7	23·6	22·25	20·65	18·75	16·75	14·70	12·30
81·27	34·0	28·3	26·8	24·5	22·07	19·55	17·13	14·60	11·80
83·98	39·0	29·9	27·7	25·3	22·5	19·7	17·1	14·4	11·60
89·75	45·0	30·5	27·4	24·0	20·8	17·6	14·8	12·0	9·25

An attempt was made to carry out a set of determinations in pure pyridine, and the molecular conductivity of an *N*/8 solution at 0° and 25° was found to be 1·51 and 2·26. It was impossible to perform a set of dilutions, as the pyridine absorbed traces of moisture very rapidly, and the addition of small quantities of water was found to exert a considerable influence on the conductivity of the lithium nitrate solution. For instance, the addition of 0·1 per cent. of water to the solution in pure pyridine increased the conductivity by 33 per cent. The unavoidable absorption of moisture during the dilutions would thus have rendered the results valueless. The very low conductivity of lithium salts dissolved in pyridine was noticed by von Laszczynski and von Gorski (*Zeitsch. Elektrochem.*, 1897, **4**, 290).

As the accuracy of the values given for the conductivity in the more dilute solutions depends to a great extent on the accuracy with which the solvent correction was determined, great care had to be taken to check this at intervals, as the conductivity of pyridine mixtures, particularly of those containing a small percentage of pyridine, changes very quickly on exposure to atmospheric carbon dioxide.

The following table gives some idea of the relative importance of the solvent corrections in the various mixtures :

TABLE X.—*Specific Conductivity of Pyridine-Water Mixtures.*

Molecular percentage of pyridine :	0·00	5·91	14·47	31·28	40·64	46·67	54·35	63·77	73·76	81·27	83·98	89·75	100·00
Specific conductivity at 0° in gemmhos :	1·5	4·6	3·1	1·8	1·1	0·7	1·1	0·3	0·6	0·5	0·4	0·3	0·2
Specific conductivity at 25° in gemmhos :	2·2	8·5	5·7	4·1	2·3	1·2	1·2	0·6	0·7	0·9	0·6	0·4	0·3

It will be noticed that the numbers do not always show a regular variation with composition, as in some cases the mixture had been kept longer than in others, and had absorbed traces of carbon dioxide.

In the case of solutions at 0°, the value of the molecular conductivity at infinite dilution is clearly indicated by the form of the curve (see Fig. 7) until the mixture containing 73·76 molecules per cent. of pyridine is reached, but beyond that it is only approximate.

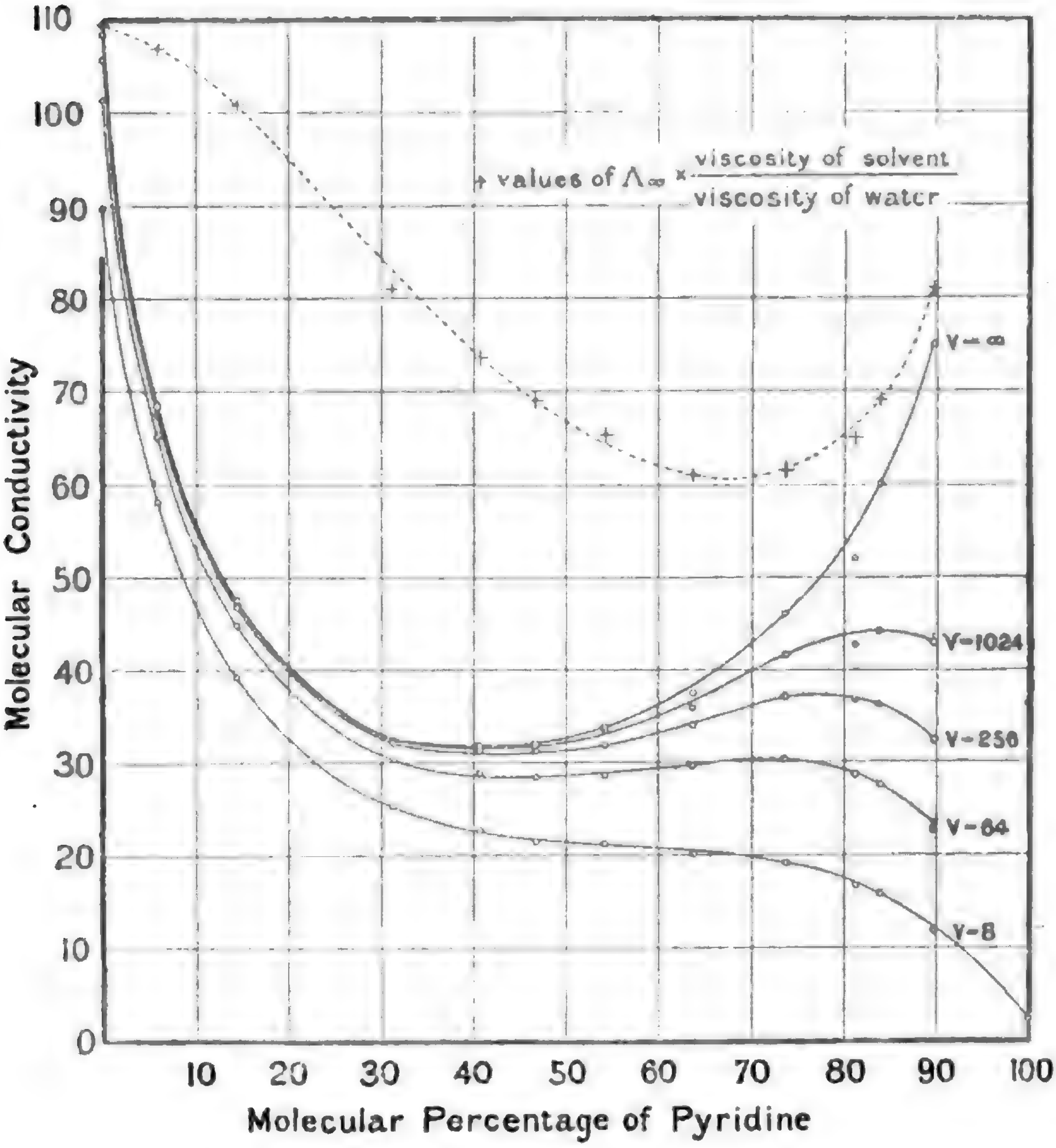
At 25°, more difficulty was found with the solvent correction, and, ionisation being less complete than at 0°, the numbers given for infinite dilutions are not so accurate, but as far as 65 molecules per cent. of pyridine they involve only a small amount of extrapolation.

In order to show the influence of the solvent and of the concentration on the molecular conductivity, curves have been drawn giving the values of Λ at dilutions $v = \infty$, 64, 256, 1024, and $_\infty$ at 0° and 25° in Figs. 8 and 9.

At infinite dilution, the molecular conductivity falls to a minimum in the neighbourhood of 40 molecules per cent. of pyridine and then rises again, the direction of the curve indicating that in pure pyridine it would have a value not far removed from that found in water.

At lower dilutions, the curves are less simple, the alterations in their form being largely due to the falling off in ionisation as the solvent becomes rich in pyridine. For instance, at 0° the values at dilution $v=8$ fall to a minimum at 41 molecules per cent., rise again to a maximum at 74 molecules per cent. of pyridine, and then fall again until the pyridine end is reached. At 25°, at the same dilution, the maximum and minimum have disappeared, and the curve shows a point of inflexion at 60 molecules per cent. of pyridine.

FIG. 8.



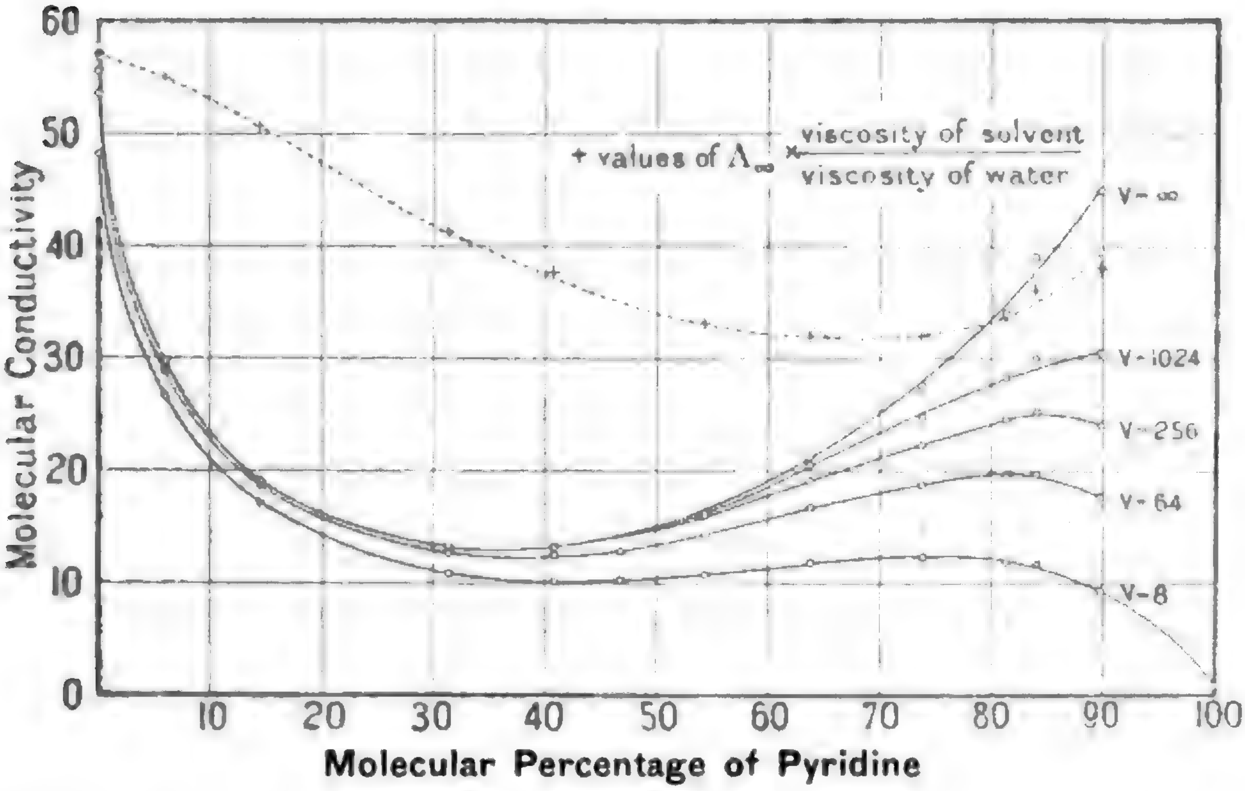
The causes of these complex variations are discussed later (p. 558).

Discussion of Results.

1. *Molecular Conductivity at Infinite Dilution.*—It has been shown by Bousfield (*Zeitsch. physikal. Chem.*, 1905, **53**, 257; *Phil. Trans.*, 1906, *A*, **206**, 101) and by Pellat (*Compt. rend.*, 1907, **144**, 902) that the application of Stokes' theorem respecting the limiting velocity of a small sphere moving under a constant force in a viscous medium to the motion of ions in solutions is of great value in studying the various causes which may affect the mobility of an ion.

The limiting velocity of a small sphere of radius, r, moving in a medium of viscosity, η, under a constant force, p, is proportional to $\frac{p}{r\eta}$. If we apply this to the case of an ion moving with a spherical solvent atmosphere surrounding it, the mobility of the ion will depend on the viscosity of the solution and of the size of the solvent envelope. Thus the three factors which determine the conductivity of a solution containing two univalent ions are: (1) the coefficient of ionisation; (2) the viscosity of the solution, and (3) the average size of the solvent atmosphere surrounding the two ions.

FIG. 9.



If we consider the same pair of ions in various solvents, such as a series of mixtures of pyridine and water, differences of ionisation are eliminated at infinite dilution, and any changes in the value of molecular conductivity in the different mixtures must be due to differences in viscosity or in the solvent atmospheres attached to the ions.

If U_a and U_k are the absolute velocities of anion and cation under unit potential gradient, r_a and r_k the average radii of the two ions, and η the viscosity of the solvent:

then $U_a = C\frac{1}{r_a . \eta}$, and $U_k = C\frac{1}{r_k . \eta}$, where C is a constant for univalent ions, and, since $\Lambda_\infty = Q(U_a + U_k)$, where Q is the charge liberated by 1 gram-equivalent of a univalent ion,

$$\therefore\ \Lambda_\infty = \frac{QC}{\eta}\left(\frac{1}{r_a} + \frac{1}{r_k}\right).$$

If r_a and r_k do not vary with the composition of the solvent, then $\Lambda_\infty \times \eta$ must remain constant, any variation in this quantity indicates a change in the size of the solvent envelopes attached to the ions.

The values of Λ_∞ × viscosity of solvent relative to water have been collected in table XI for 0° and 25°, and they are plotted on the dotted curve in Figs. 8 and 9 (relative, instead of absolute, values of the viscosity were taken for convenience in plotting on the same scale as the rest of Figs. 8 and 9):

TABLE XI.—*Molecular Conductivity at Infinite Dilution, Viscosity, and* $\Lambda_\infty \times \frac{\eta\text{-solvent}}{\eta\text{-water}}$ *for Lithium Nitrate Solutions in Pyridine–Water Mixtures at* 0° *and* 25·08°.

	Values at 0°.			Values at 25°.		
Molecular percentage of pyridine in solvent.	Molecular conductivity at infinite dilution.	Viscosity in absolute units.	$\Lambda_\infty \times \frac{\eta\text{-solvent}}{\eta\text{-water}}$.	Molecular conductivity at infinite dilution.	Viscosity in absolute units.	$\Lambda_\infty \times \frac{\eta\text{-solvent}}{\eta\text{-water}}$
0·00	57·10	0·01778	57·1	109·4	0·00890	109·4
5·91	29·85	0·03280	55·0	68·5	0·01389	106·9
14·47	19·05	0·04735	50·7	47·5	0·01890	100·9
31·28	13·25	0·05535	41·3	32·4	0·02226	81·0
40·64	13·40	0·04990	37·6	31·8	0·02060	73·6
46·67	—	—	—	32·0	0·01920	69·0
54·35	16·25	0·03625	33·1	33·9	0·01713	65·3
63·77	21·2	0·02670	32·0	37·5	0·01451	61·0
73·76	27·5	0·02055	32·0	46·0	0·01194	61·5
81·27	34·0	0·01745	33·5	54·0	0·01065	65·0
83·98	39·0	0·01645	36·0	60·0	0·01029	69·0
89·75	45·0	0·01485	38·0	75·0	0·00964	81·0

The form of the curves shows that at both temperatures, as the amount of pyridine in the solvent increases, the atmospheres attached to one or both ions increase also until the solvent contains about 67 molecules per cent. of pyridine, at which concentration the increased loading of the ions has been such as to reduce the sum of the mobilities of the ions to about 56 per cent. of their value in water. The agreement between the two temperatures both as to the position of the minimum and as to the calculated change of atmosphere is rather striking.

After 67 molecules per cent. of pyridine, the atmospheres decrease again in both cases, and the direction of the curves indicate that in pure pyridine they would return to a value approximately the same as in water. As we were not able to determine the transport numbers of the two ions, we can only consider the collective effect on their mobilities.

2. *Coefficient of Ionisation.*—The ordinary equation used in calculating the coefficient of ionisation:

$$a = \frac{\Lambda_v}{\Lambda_\infty},$$

neglects changes in the mobilities of the ions at different concentrations due to changes in the viscosity of the solution, and to variations in the size of the solvent atmosphere attached to them (Bousfield, *loc. cit.*). In the case of dilute aqueous solutions (between $v = 8$ and 1024), the changes in viscosity are relatively small, and may be neglected except in the most accurate work, but, in the case of solutions in pyridine–water mixtures, reference to the viscosity curve in Figs. 3 and 4 will show that these viscosity changes are much greater, and must be taken into account in calculating a. Assuming that the mobility of the ion varies inversely with the viscosity of the medium, we have calculated a by the formula:

$$a = \frac{\Lambda_v}{\Lambda_\infty} \times \frac{\text{viscosity of solution}}{\text{viscosity of solvent}}.$$

The numbers obtained in this way are given in the following tables for 0° and 25°:

TABLE XII.—*Coefficients of Ionisation in Lithium Nitrate Solutions at 25·08°.*

Molecular percentage of pyridine in solvent.	Coefficient of ionisation.							
	V=1024.	512.	256.	128.	64.	32.	16.	8.
0·00	0·993	0·980	0·966	0·949	0·928	0·902	0·870	0·832
5·91	0·999	0·996	0·988	0·972	0·954	0·931	0·905	0·876
14·47	0·998	0·994	0·988	0·974	0·950	0·925	0·896	0·862
31·28	1·000	1·000	0·993	0·973	0·945	0·909	0·869	0·824
40·64	0·995	0·994	0·982	0·952	0·915	0·874	0·826	0·778
46·67	0·998	0·992	0·978	0·943	0·898	0·850	0·796	0·734
54·35	0·989	0·969	0·941	0·905	0·853	0·796	0·746	0·682
63·77	0·955	0·945	0·909	0·855	0·798	0·738	0·664	0·578
73·76	0·905	0·860	0·805	0·740	0·665	0·590	0·520	0·455
81·27	0·79	0·73	0·68	0·61	0·53	0·47	0·40	0·34
83·98	0·74	0·67	0·60	0·54	0·47	0·40	0·34	0·29
89·75	0·57	0·50	0·43	0·36	0·31	0·26	0·21	0·17

TABLE XIII.—*Coefficients of Ionisation in Lithium Nitrate Solutions at 0°.*

Molecular percentage of pyridine in solvent.	Coefficient of ionisation.							
	$V = 1024$.	512.	256.	128.	64.	32.	16.	8.
0·00	0·997	0·990	0·976	0·960	0·940	0·915	0·882	0·847
5·91	1·000	0·997	0·993	0·983	0·969	0·950	0·927	0·898
14·47	1·000	1·000	1·000	0·991	0·981	0·964	0·939	0·910
31·28	1·000	1·000	0·994	0·981	0·958	0·933	0·902	0·864
40·64	0·998	0·994	0·987	0·971	0·942	0·902	0·857	0·805
54·35	0·991	0·989	0·978	0·943	0·889	0·832	0·775	0·716
63·77	0·970	0·945	0·900	0·850	0·795	0·740	0·680	0·605
73·76	0·915	0·875	0·825	0·770	0·705	0·640	0·580	0·510
81·27	0·83	0·79	0·72	0·65	0·58	0·52	0·45	0·38
83·98	0·77	0·71	0·65	0·58	0·51	0·45	0·39	0·33
89·75	0·68	0·61	0·54	0·47	0·40	0·34	0·28	0·23

We were unable to take account of the variation of ionic size with dilution, but Bousfield's results indicate that this would not be large within the range over which we worked.

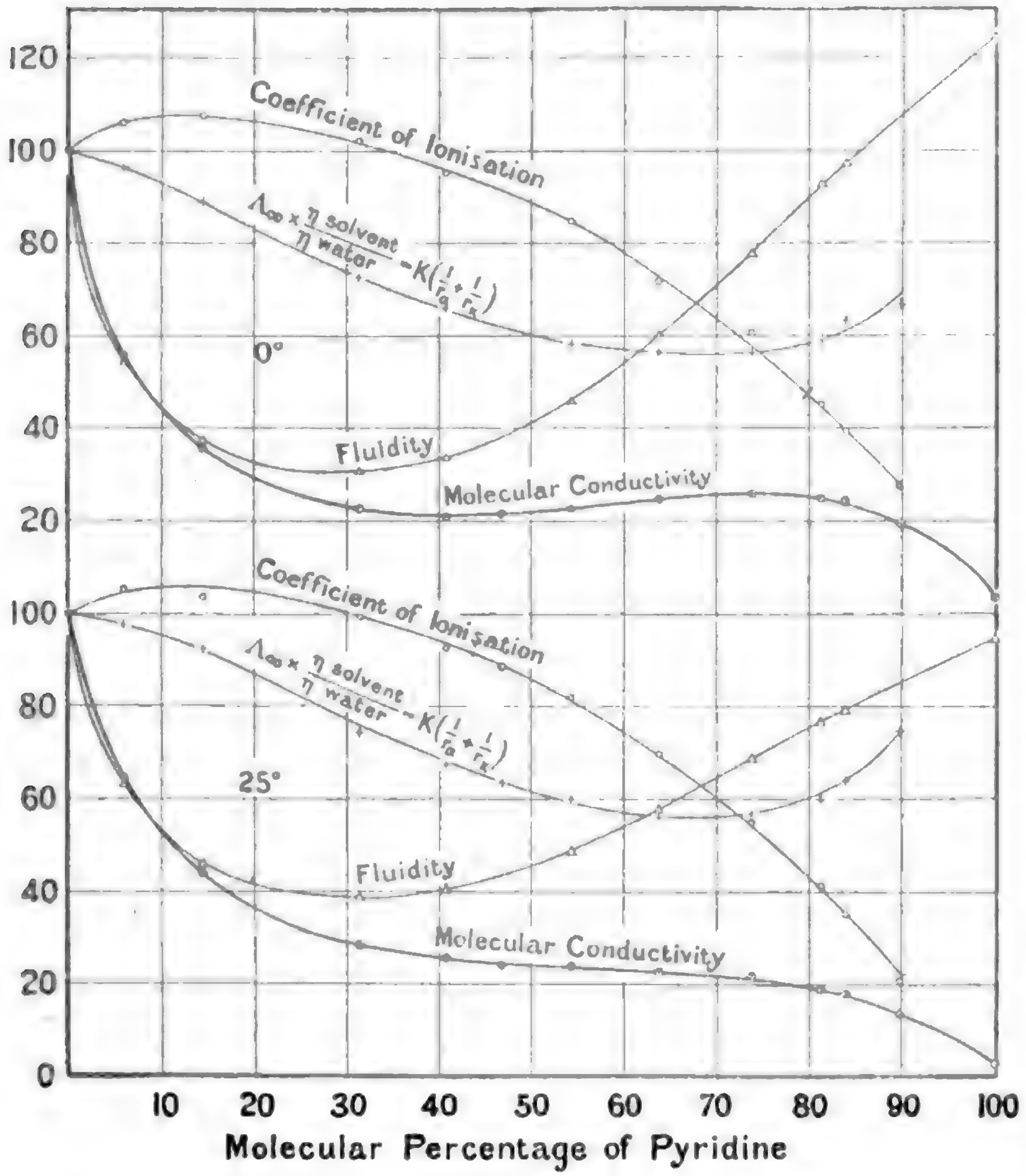
It will be seen that in all cases, ionisation is more complete at the lower temperatures and that dilute pyridine solutions in water have a greater dissociating power than water itself, but, as the proportion of pyridine increases, the ionisation quickly falls off.

Having now traced the effects due to viscosity, ionic size, and ionisation, we can examine the causes which have determined the form of the molecular conductivity curve given in Figs. 8 and 9. If we consider the variations of viscosity and of the ionic atmospheres with solvent composition, we see that their joint effect must tend to produce a minimum value of the molecular conductivity in the solvent containing about 40 molecules per cent. of pyridine, as is the case at infinite dilution; at all other dilutions, this effect is further complicated by variations in the coefficient of ionisation, thus explaining why all the curves except those for Λ_∞ show either a minimum and a maximum (compare Λ_{64} at 0° and 25°) or a point of inflexion (compare Λ_8 at 25°).

In order to show the relative importance of each of the three factors, Fig. 10 has been constructed, in which the thick curves give the relative values for Λ_8 at 0° and 25° in various solvent mixtures, and the three other curves give the relative values of the coefficient of ionisation, of the quantity $\Lambda_\infty \times \dfrac{\eta\text{-mixture}}{\eta\text{-H}_2\text{O}}$, and of the fluidity of the solution, the water value being put at 100 in each case for purposes of a convenient comparison.

It is seen that at 0° the molecular conductivity falls off quickly, owing to the decrease in fluidity and the increasing atmospheres carried by the ions, the falling off being partly counteracted by an increase in the coefficient of ionisation ; at 41 molecules per cent. of pyridine, the value of Λ_8 reaches a minimum, and the subsequent increase is due to an increase in liquidity, which is slightly helped by a decrease in the size of the ionic atmospheres, but the increase is checked at 74 molecules per cent. of pyridine, owing to the rapid falling off of the ionisation and Λ_8 decreases until in pure pyridine it is only 3 per cent. of its value in water.

FIG. 10.



At 25°, the curve for Λ_8 falls off gradually with a point of inflexion in the neighbourhood of 60 molecules per cent. of pyridine, as, owing to the changes in fluidity and the values of *a* being smaller than in the solution at 0°, there is no minimum and maximum in the middle part of the curve.

Results.

1. The density-concentration curves for mixtures of water and pyridine have been traced at 0° and 25·08°, both curves showing a maximum deviation from the line joining the end values in the neighbourhood of 30 molecular percentages of pyridine.
2. The viscosity-concentration curves for similar mixtures have been traced at the same temperatures, the maximum deviation again occurring in the neighbourhood of 30 molecular percentages of pyridine at both temperatures.
3. In neither of the above cases was any evidence found of the existence of the discontinuities mentioned by Dunstan, Thole, and Hunt (*loc. cit.*).
4. The surface tension of mixtures of pyridine and water has been determined at 0° and 25°, and the "surface excess" of pyridine in dilute solutions has been calculated to be 0·16 milligram per sq. metre, corresponding with an increase of concentration of 3·2 milligrams per c.c. in the surface layer.
5. The molecular conductivity of lithium nitrate dissolved in pyridine–water mixtures has been determined at 0° and 25° at dilutions varying from $v=8$ to $v=1024$, and the values at infinite dilution have been obtained by extrapolation.
6. The variation of the sum of the ionic mobilities at infinite dilution, due to changes in the size of the solvent atmospheres attached to the ions, has been estimated for these solutions by means of Stokes's theorem.
7. It has been shown that the form of the molecular conductivity curves for these solutions may be explained as the result of variations in the coefficient of ionisation, the fluidity of the solution, and the aggregation of solvent particles round the ions.

We intend to continue this investigation.

We desire to express our best thanks to the Research Fund Committee of the Chemical Society for a grant which defrayed part of the expenses of this investigation, and also to Mr. D. H. Nagel, M.A., Trinity College, Oxford, for much valuable advice during the progress of the work.

PHYSICAL CHEMISTRY LABORATORY,
BALLIOL COLLEGE AND TRINITY COLLEGE,
OXFORD.

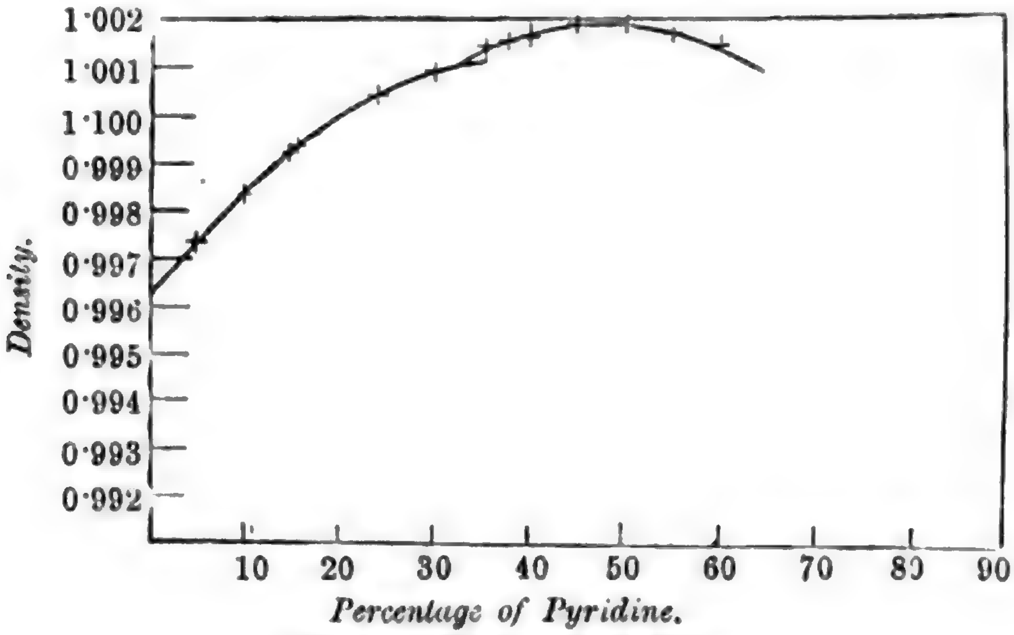
LI.—*The Viscosity of Aqueous Pyridine Solutions.*

By ALBERT ERNEST DUNSTAN and FERDINAND BERNARD THOLE.

IN the preceding paper (compare also Proc., 1908, **24**, 22), Hartley, Thomas, and Applebey, dealing with the viscosity of aqueous solutions of pyridine, point out that the results they obtained showed considerable discrepancies when compared with those brought forward by Dunstan, Thole, and Hunt (Trans., 1907, **91**, 1728), in that the latter authors had represented the viscosity curve as discontinuous, whereas they found that their experimental points lay on a smooth curve.

It is obvious that, although for the sake of clearness the curve obtained by Dunstan, Thole, and Hunt was shown in discontinuous sections, yet could sufficient points be determined, each section would gradually merge into the next. In reality, the discontinuous extremities are of the nature of tangential prolongations of the actually continuous sections of the curve.

FIG. 1.



(Drawn with the aid of lath.)

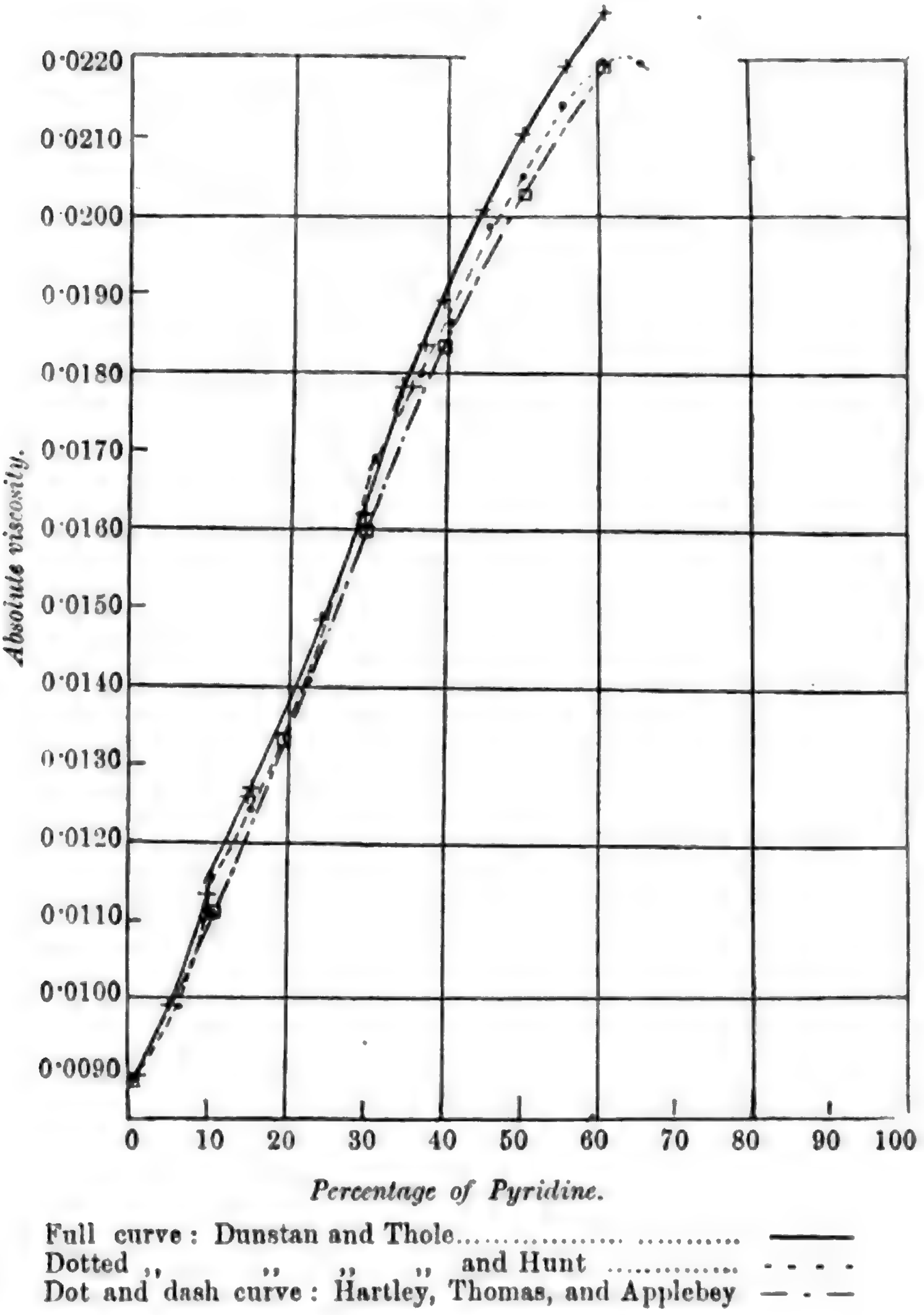
The present authors, however, thought it advisable to repeat their work up to concentrations of 60 per cent. of pyridine, for beyond this point their curve agrees sufficiently well with that of Hartley, Thomas, and Applebey.

The following are the numbers obtained :

Percentage of pyridine.	Density $^{25}/_{4}$.	Viscosity.	Percentage of pyridine.	Density $^{25}/_{4}$.	Viscosity.
0·0	0·9972	0·00891	35·49	1·0023	0·01778
4·98	0·9983	0·09910	37·67	1·0025	0·01830
10·01	0·9993	0·01135	40·18	1·0025	0·01884
15·09	1·0002	0·01262	45·03	1·0027	0·02005
15·57	1·0003	0·01270	50·03	1·0028	0·02106
23·87	1·0014	0·01485	55·19	1·0026	0·02194
30·02	1·0018	0·01620	60·08	1·0024	0·02259
35·23	1·0025	0·01780	100·00	0·9763	0·00879

The new curve, Fig. 1, agrees very well with the original one. There are the same "discontinuities" at about 10 per cent. and 32 per cent. of pyridine, although the material used (obtained by distilling Kahlbaum's purest product over potassium hydroxide) had a slightly higher boiling point, 116°/782 mm., and a lower density, namely, 0·9763, than our previous sample (114·4—114·8°/758 mm. and 0·9783).

FIG. 2.



As a matter of fact, it should be mentioned that our original curve and Hartley, Thomas, and Applebey's are by no means strikingly discrepant, for fourteen of our points lie on or very near to his curve and only two are well off it. Moreover, we made a larger number of determinations and drew our curve by the aid of a flexible lath. The difference is really a matter of interpretation of results: whether it is valid or not to regard as permissible the existence of "sections" in a curve connecting a physical property and percentage composition. This we submit is a matter for individual judgment.

It should, however, be borne in mind that the "discontinuities" are very small in comparison with the general appearance of the curve, and are of slight importance so far as our general conclusions are concerned. Quite recently, Kremann (*Monatsh.*, 1907, **28**, 831) in an elaborate survey of the question as to the existence of molecular compounds in solution has accepted these conclusions and confirmed them by a considerable amount of experimental data. Hartley, Thomas, and Applebey's work also confirms our conclusion that pyridine–water falls into Class II of our system.

Further support is afforded by the work of Holmes (Trans., 1906, **89**, 1774), who obtained a density curve for pyridine–water which is distinctly discontinuous.

Lastly, Hartley, Thomas, and Applebey's own results show a discontinuity at approximately the same position as one of ours (see Fig. 2), although it is difficult to find the others, owing to the lack of sufficient points.

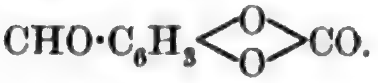
EAST HAM TECHNICAL COLLEGE,
EAST HAM, E.

LII.—*The Action of Thionyl Chloride and of Phosphorus Pentachloride on the Methylene Ethers of Catechol Derivatives.*

By GEORGE BARGER.

THE synthesis of compounds containing an ortho-dihydroxybenzene nucleus is generally attended with difficulty owing to the instability of this nucleus. On the other hand, the methylene ethers of many such compounds are easily obtainable from piperonal, which substance, like benzaldehyde, readily undergoes a variety of reactions. The transformation of the methylene ethers into the phenolic compounds presents, however, considerable difficulty. Although the methylene group is somewhat more easily removed than methyl groups, the usual reagents for the preparation of phenolic compounds from the corresponding alkyl ethers generally bring about the disruption of the molecule, when applied to catechol derivatives. One of the few examples of the successful application of such reagents is the preparation of protocatechualdehyde from piperonal by heating with dilute hydrochloric acid or with acid salts to 150—190° (D.R.-P. 16784 of 1904).

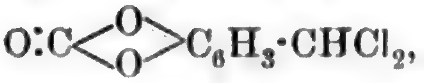
A peculiar reaction of the methylene ethers of catechol derivatives was discovered long ago by Fittig and Remsen (*Annalen*, 1871, **159**, 144), and applied by them to piperonal and to piperonylic acid. By heating the former substance with phosphorus pentachloride, they obtained a tetrachloro-derivative, which undoubtedly has the constitution $Cl_2{:}C{:}O_2{:}C_6H_3{\cdot}CHCl_2$. By treatment with cold water, two chlorine atoms are replaced by an oxygen atom, and, according to Fittig and Remsen, this substance, termed dichloropiperonal, has the constitution $Cl_2{:}C{:}O_2C_6H_3{\cdot}CHO$. By boiling water it is hydrolysed to carbon dioxide, hydrochloric acid, and protocatechualdehyde.

Recently, Pauly (*Ber.*, 1907, **40**, 3096) has examined this reaction more closely, and described an interesting intermediate compound. He, for the first time, obtained dichloropiperonal quite pure (by distillation under reduced pressure) and was further able to replace the remaining pair of chlorine atoms of this substance by an oxygen atom (by heating with anhydrous oxalic acid, and by other means). Pauly thus obtained the cyclic carbonate of protocatechualdehyde,  $CHO{\cdot}C_6H_3{<}{}^{O}_{O}{>}CO$. When boiled with water, this substance breaks up into carbon dioxide and protocatechualdehyde, and, for this reason, escaped the notice of Fittig and Remsen.

With the view of preparing other catechol compounds from the corresponding methylene ethers, the author was led to investigate the action of thionyl chloride, in consideration of the fact that the latter substance has often shown itself superior to phosphorus pentachloride in the preparation of acid chlorides. In a preliminary experiment, thionyl chloride was caused to act on piperonal. Up to 150°, scarcely any action took place, but at 180° an almost quantitative yield of "dichloropiperonal" was obtained on removal of the excess of thionyl chloride employed. The effect of heating with thionyl chloride was therefore the same as heating with phosphorus pentachloride, and subsequent treatment with cold water. When substances containing two catechol nuclei were employed, such as piperonyloin, some difficulty was at first experienced in interpreting the reaction. By heating with thionyl chloride, piperonyloin yielded a substance containing only two chlorine atoms. Since boiling water converted the dichloro-compound into a substance with two free catechol nuclei,* both methylene groups had been attacked (as, indeed, one might expect). On Fittig and Remsen's view, the substance should therefore have contained four chlorine atoms, and the question arose whether "dichloropiperonal" is not in reality the cyclic carbonate of piperonylidene chloride, and whether it should not be formulated as

---

* An account of these and similar substances will be published later.



$$O{:}C<^{O}_{O}>C_6H_3{\cdot}CHCl_2,$$

instead of $Cl_2{:}C<^{O}_{O}>C_6H_3{\cdot}CHO$, as supposed by Fittig and Remsen (and also by Pauly). Further experiments seem to leave no doubt that the former constitution is the correct one. That thionyl chloride, or phosphorus pentachloride and cold water, transforms methylene ethers of catechol derivatives into the corresponding cyclic carbonates was proved by their action on methylenedioxybenzene itself, and on piperonylic acid. Phosphorus pentachloride converts methylenedioxybenzene into a chloro-derivative of the probable constitution $Cl_2{:}C<^{O}_{O}>C_6H_4$, and this is changed by cold water to a chlorine-free substance, the cyclic carbonate of catechol, $O{:}C<^{O}_{O}>C_6H_4$, which has already been prepared by the action of carbonyl chloride on the sodium derivative of catechol.

The action of phosphorus pentachloride on piperonylic acid has already been investigated by Fittig and Remsen. According to these authors, cold water converts the crude liquid product of the reaction into a solid chloro-acid, to which they assigned the constitution $Cl_2{:}C{:}O_2{:}C_6H_3{\cdot}CO_2H$. Since the chlorine content of the (somewhat impure) preparation corresponded more closely with one atom of chlorine only, they suggested that a further change takes place under the influence of cold water, resulting in a substance of the constitution $^{HO}_{Cl}>C<^{O}_{O}>C_6H_3{\cdot}CO_2H$, but owing to the poor agreement of their analytical results with the calculated values, they did not attach much importance to this suggestion. The explanation is now, however, obvious. The supposed chloro-acid was in reality the cyclic carbonate of protocatechuoyl chloride, $O{:}C<^{O}_{O}>C_6H_3{\cdot}COCl$, and the carbon and hydrogen content found by Fittig and Remsen agrees closely with that required by the above formula:

Found (by Fittig and Remsen), C = 48·43; H = 2·01.

$C_8H_3O_4Cl$ requires C = 48·36; H = 1·51 per cent.

The chlorine found by them was somewhat low, 16·81 instead of 17·88 per cent., as might have been expected after treatment of an acid chloride with water.

The behaviour of the substance towards hydroxyl and amino-groups agrees in every respect with that of an aromatic acid chloride, and leaves no doubt as to its constitution. It has been employed in the synthesis of new catechol derivatives, a number of which are described below.

In accordance with what has been said above, the carbonate of protocatechuoyl chloride should be produced directly from piperonylic acid by the action of thionyl chloride at 180°, and this was indeed found to be the case. On removal of the excess of thionyl chloride in a vacuum, the acid chloride remains behind as a crystalline mass, and it was in this experiment that its true nature was first recognised.

The direct production of cyclic carbonates by successive treatment of methylene ethers with phosphorus pentachloride and with cold water has already been observed by Delange (*Compt. rend.*, 1904, **138**, 423 and 1701) who obtained in this way the cyclic carbonates of 3:4-dihydroxy-1-ethyl-, -*a*-1-propyl-, and -1-*iso*propyl-benzene.

It seems safe to conclude from the above evidence that the two chlorine atoms which are introduced by phosphorus pentachloride into the methylene group are much more labile than any other chlorine atoms which may be introduced at the same time into another part of the molecule. By cold water, moist air, anhydrous formic acid, glacial acetic acid, or acetic anhydride (Delange) they are replaced by an oxygen atom; thionyl chloride introduces this oxygen atom at the outset. The violence with which these two chlorine atoms react with hydroxyl- and amino-groups is without parallel among aromatic chloro-compounds, although not surprising if we regard the substances in question as the dichlorides of an ethereal salt of orthoformic acid. If we consider that benzylidene chloride requires heating with water to 140—160° in order to convert it into benzaldehyde, we should not expect the carbonate of dihydroxybenzylidene chloride to react with cold water. The two chlorine atoms, which Pauly replaced by an oxygen atom in the production of protocatechualdehyde carbonate, are therefore those of the aldehyde group and not, as he seems to imagine, those in the carbonyl (methylene) group.

EXPERIMENTAL.

Conversion of Methylenedioxybenzene into Carbonyldioxybenzene.

1·45 Grams of crude methylenedioxybenzene, b. p. 170—180°, containing a little methylene iodide, and obtained by the action of methylene iodide on disodium catechol (Moureu, *Bull. Soc. chim.*, 1896, [iii], **15**, 655) were heated for half an hour under a reflux condenser with 3·5 grams (2 mols.) of phosphorus pentachloride.

After removal of the phosphorus trichloride by distillation at atmospheric pressure, the dichloromethylenedioxybenzene, $Cl_2{:}CO_2{:}C_6H_4$, distilled in a vacuum at about 90°. On treating the distillate with cold water, hydrogen chloride was evolved and 0·75 gram of a white, chlorine-free solid resulted, which, when crystallised from benzene, melted at 119°. The melting point was not changed by mixing with a specimen of carbonyldioxybenzene (obtained by means of carbonyl chloride). The latter specimen melted at 119·5°.

Action of Thionyl Chloride on Piperonyl Alcohol.

Two grams of piperonyl alcohol * were dissolved in 6 c.c. of thionyl chloride; an energetic reaction took place at once (formation of piperonyl chloride), and the solution was then heated in a sealed tube to 180° for seven hours. After removal of the excess of thionyl chloride, the product of the reaction distilled at 165—183°/12 mm. On boiling the distillate with formic acid, a more than 50 per cent. yield of 3:4-carbonyldioxybenzoic acid was obtained. The piperonyl chloride had therefore been oxidised to carbonyldioxybenzoyl chloride,

$$O{:}C{:}O_2{:}C_6H_3{\cdot}COCl$$

(b. p. 166—167°/13 mm.).

The action of thionyl chloride on benzyl alcohol at 180° was next examined, and found to be completely analogous. The product of the reaction was evidently a mixture of benzyl and benzoyl chlorides, and the highest fraction, boiling at 198°, yielded benzoic acid.

Phosphorus pentachloride acting on piperonyl alcohol produced a tar from which nothing could be isolated.

3 : 4-*Carbonyldioxybenzoyl Chloride*, $O{:}C{:}O_2{:}C_6H_3{\cdot}COCl$.

Piperonylic acid heated with an excess of thionyl chloride on the water-bath furnishes piperonyl chloride, melting at 80°, and boiling at 140—141°/8 mm., which has already been prepared by Perkin and Robinson (*Proc.*, 1905, **21**, 287) by means of phosphorus trichloride. At a higher temperature, thionyl chloride forms 3 : 4-carbonyldioxybenzoyl chloride, the methylene group being also attacked.

Two grams of piperonylic acid were heated with 6 c.c. of thionyl chloride to 180—200° for eight hours. On distilling off the excess of thionyl chloride in a vacuum on the water-bath, a pale brown, viscous liquid remained, which crystallised on cooling, and distilled at 166—167°/12 mm. On crystallisation from a mixture of benzene and light petroleum, it melted at 68°:

---

* The piperonyl alcohol and piperonylic acid employed in these experiments were prepared from piperonal by Cannizzaro's reaction. Aqueous potassium hydroxide was found to be much better than alcoholic, as used by Decker and Koch (*Ber.*, 1905, **39**, 1741), since it gave a larger yield of a purer product. Fifty-six grams of piperonal, mixed with 36 grams of potassium hydroxide dissolved in 24 grams of water, gave, after standing 24 hours at the laboratory temperature, 28 grams of the acid and 22 grams of the alcohol (m. p. 52—53°).

0·1828 gave 0·3278 CO_2 and 0·0276 H_2O. C = 48·5; H = 1·7.
0·1483 „ 0·1044 AgCl (by boiling with water). Cl = 17·4.
$C_8H_3O_4Cl$ requires C = 48·4; H = 1·5; Cl = 17·9 per cent.

The compound was also prepared by heating piperonylic acid with three molecular proportions of phosphorus pentachloride under a reflux condenser for several hours, and gradually distilling off the phosphorus trichloride and phosphoryl chloride through a fractionating column, so that the temperature of the residual liquid at last rose to 160°. On distillation, a little phosphorus pentachloride sublimed, and then the product of the reaction distilled at 149—150°/12 mm. It was not quite pure, as the reaction was incomplete, some unchanged piperonyl chloride being present. (Found: Cl = 39·2; $C_8H_3O_3Cl_3$ requires Cl = 42·0 per cent.)

After the substance had been freed from phosphorus halides, it no longer reacted readily with cold water, on account of its insolubility, and it was not found possible to convert it easily into a solid product by Fittig and Remsen's method. When dissolved in acetone, it reacted violently with water, so that the acetone was raised to its boiling point. The most convenient method of transformation into 3 : 4-carbonyldioxybenzoyl chloride was found to be prolonged exposure in a thin layer to moist air, when in the course of one or two days the substance was completely transformed into a hard, crystalline mass, which, when recrystallised from benzene and light petroleum, was found to be identical with the substance obtained by thionyl chloride direct.

The constitution of the substance is proved by its transformation to 3 : 4-carbonyldioxybenzoic acid and its derivatives; all these substances can be further changed to the corresponding derivatives of protocatechuic acid by boiling with water.

3 : 4-*Carbonyldioxybenzoic Acid*, $O:C:O_2:C_6H_3\cdot CO_2H$.

When 3 : 4-carbonyldioxybenzoyl chloride is heated with a little anhydrous formic acid, it readily dissolves, but soon an energetic reaction begins; hydrogen chloride is evolved and 3 : 4-carbonyldioxybenzoic acid separates. By using enough formic acid to keep the substance in solution and boiling for a short time, the latter at once crystallises out in a condition of analytical purity. Glacial acetic acid may be used instead of formic acid, and dichloropiperonyl chloride may be employed instead of carbonyldioxybenzoyl chloride:

0·1687 gave 0·3289 CO_2 and 0·0365 H_2O. $C=53·2$; $H=2·4$.
$C_8H_4O_5$ requires $C=53·3$; $H=2·2$ per cent.

3 : 4-*Carbonyldioxybenzoic acid* melts at 228° with effervescence. It is insoluble in water, and somewhat sparingly soluble in most organic solvents in the cold. Its alcoholic solution is not coloured by ferric chloride. On boiling the acid with water or with salt solution, it is quantitatively converted into protocatechuic acid, which separates in white crystals melting at 197—198°.

Methyl 3 : 4-*Carbonyldioxybenzoate*, $O{:}C{:}O_2{:}C_6H_3{\cdot}CO_2{\cdot}CH_3$.

This substance was prepared by dissolving the acid chloride in methyl alcohol without rise of temperature. On the addition of water, crystals separated melting at 90° :

0·1752 gave 0·3549 CO_2 and 0·0495 H_2O. $C=55·4$; $H=3·1$.
$C_9H_6O_5$ requires $C=55·7$; $H=3·2$ per cent.

Methyl 3 : 4-*carbonyldioxybenzoate* is very soluble in most organic solvents, and does not give a reaction with ferric chloride. By boiling with water or making alkaline with ammonia, it is changed to methyl protocatechuate, which could, however, not be obtained quite pure owing to further decomposition, resulting in the formation of protocatechuic acid.

Phenyl-3 : 4-*carbonyldioxybenzoate*, $O{:}C{:}O_2{:}C_6H_3{\cdot}CO_2{\cdot}C_6H_5$.

Equimolecular proportions of phenol and of 3 : 4-carbonyldioxybenzoyl chloride were heated together, until the evolution of hydrogen chloride ceased. A little benzene was then added to the hot liquid and, on cooling, *phenyl* 3 : 4-*carbonyldioxybenzoate* crystallised in stout crystals, melting at 126° :

0·1433 gave 0·3458 CO_2 and 0·0405 H_2O. $C=65·8$; $H=3·1$.
$C_{14}H_8O_5$ requires $C=65·6$; $H=3·1$ per cent.

Phenyl Protocatechuate, $(OH)_2C_6H_3{\cdot}CO_2{\cdot}C_6H_5$.

The substance just described was suspended in boiling water, and dilute ammonia was added drop by drop until all was dissolved. If an excess is avoided, the solution scarcely darkens at all. After filtration, dilute hydrochloric acid was added drop by drop to the hot solution, so that crystals of phenyl protocatechuate separated out. The substance was recrystallised from very dilute alcohol and then melted at 189°. It is readily soluble in cold alcohol, but almost insoluble in boiling water; its solution is coloured green by ferric chloride:

0·1090 gave 0·2717 CO_2 and 0·0438 H_2O. C = 68·0; H = 4·5.
$C_{13}H_{10}O_{14}$ requires C = 67·8; H = 4·4 per cent.

Methoxyphenyl 3 : 4-*Carbonyldioxybenzoate*, $O{:}C{:}O_2{:}C_6H_3\cdot CO_2\cdot C_6H_4\cdot O\cdot CH_3$.

Prepared like the phenyl derivative from the acid chloride and guaiacol, this substance yielded stout crystals, sparingly soluble in hot benzene and melting at 159°:

0·1402 gave 0·3255 CO_2 and 0·0442 H_2O. C = 63·3; H = 3·5.
$C_{15}H_{10}O_6$ requires C = 62·9; H = 3·5 per cent.

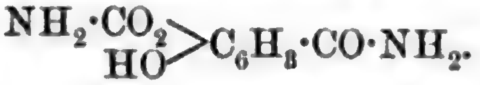
Methoxyphenyl Protocatechuate, $(OH)_2C_6H_3\cdot CO_2\cdot C_6H_4\cdot O\cdot CH_3$.

Prepared from the compound just described in the same way as the corresponding phenyl derivative, it yielded prisms melting at 194°:

0·1598 gave 0·3768 CO_2 and 0·0680 H_2O. C = 64·3; H = 4·7.
$C_{14}H_{12}O_5$ requires C = 64·6; H = 4·6 per cent.

Protocatechuamide, $(OH)_2C_6H_3\cdot CO\cdot NH_2$.

The preparation of this substance presented some difficulty owing to the instability of the carbonyl group towards ammonia. When 3 : 4-carbonyldioxybenzoyl chloride was treated with dry ammonium carbonate, a substance resulted which gave a green coloration with ferric chloride, and could not be obtained crystalline. By passing dry ammonia into the acid chloride dissolved in carefully dried benzene, a white, amorphous precipitate was immediately formed, which was collected and dried in a vacuum desiccator over paraffin wax and sulphuric acid. It was expected that the precipitate would consist of a mixture of ammonium chloride and 3 : 4-carbonyldioxybenzamide, and it was hoped that the former substance could be extracted by water. Almost the whole of the precipitate dissolved, however; on prolonged standing crystals separated. These were recrystallised from ethyl acetate, in which they were but sparingly soluble, and they then melted at 131° with effervescence. The new substance was probably a *urethane* of protocatechuic acid, having the formula:



$$\left.\begin{matrix}NH_2\cdot CO_2\\ HO\end{matrix}\right>C_6H_3\cdot CO\cdot NH_2.$$

0·1088 gave 12·3 c.c. moist nitrogen at 15·5° and 764 mm. N = 13·3.
$C_8H_8O_4N_2$ requires N = 14·3 per cent.

Protocatechuamide was, however, obtained by keeping 3 : 4-carbonyldioxybenzoyl chloride with an excess of dry liquid ammonia in a sealed tube at the laboratory temperature for two days. On allowing the excess of ammonia to evaporate at the ordinary temperature, a red solid remained, which was completely freed from ammonia in a vacuum over sulphuric acid and then crystallised from water.

The crystals were somewhat coloured and melted at 212°. With ferric chloride they gave an intense green coloration:

0·2392 gave 18·7 c.c. moist nitrogen at 5° and 770 mm. $N = 9·7$.
$C_7H_7O_3N$ requires $N = 9·2$ per cent.

3 : 4-*Carbonyldioxybenzanilide*, $O:C:O_2C_6H_3·CO·NH·C_6H_5$.

Two molecular proportions of aniline, dissolved in a little benzene, were added to 0·5 gram of 3 : 4-carbonyldioxybenzoyl chloride, dissolved in 10 c.c. of benzene. A precipitate consisting of the anilide and of aniline hydrochloride was formed. On extracting the precipitate with water, the anilide remained behind and was then crystallised from boiling alcohol and subsequently from ethyl acetate. It formed white, hair-like needles melting sharply at 214°:

0·2271 gave 11·0 c.c. moist nitrogen at 14° and 766 mm. $N = 5·7$.
$C_{14}H_9O_4N$ requires $N = 5·5$ per cent.

Protocatechuanilide, $(OH)_2C_6H_3·CO·NH·C_6H_5$.

3 : 4-Carbonyldioxybenzanilide was dissolved in pyridine and an equal volume of water was then added; bubbles of carbon dioxide were given off. After removal of most of the pyridine by distillation, white, glistening plates separated, consisting of protocatechuanilide. The hydrolysis of the carbonate can also be performed by suspending it in boiling water, and adding dilute ammonia, drop by drop, as described for phenyl protocatechuate. The substance retains water at 100° and was dried at 115° until of constant weight:

0·1441 gave 0·3591 CO_2 and 0·0606 H_2O. $C = 68·0$; $H = 4·7$.
0·3177 ,, 16·6 c.c. moist nitrogen at 14° and 766 mm. $N = 6·2$.
$C_{13}H_{11}O_3N$ requires $C = 68·1$; $H = 4·8$; $N = 6·1$ per cent.

Protocatechuanilide melts at 166—167°. It is sparingly soluble in hot water, but readily so in hot alcohol; its solutions gave the characteristic green coloration with ferric chloride. The substance has been prepared before from protocatechuic acid by Schiff (*Ber.*, 1882, **15**, 2589) and by Thibault (*Bull. Soc. chim.*, 1904, [iii], **31**, 920). The latter author criticises Schiff's method of preparation and himself gives the melting point 154—156°. The analytical figures and the melting point given above would, however, appear to refer to a purer specimen, and illustrate the advantage of preparing catechol derivatives, when possible, from the corresponding methylene ethers by way of the cyclic carbonates.

Action of Thionyl Chloride and of Phosphorus Pentachloride on Piperonal.

Two grams of piperonal were heated with 8 c.c. of thionyl chloride to 220° for seven hours. On removal of the excess of thionyl chloride in a vacuum on the water-bath, a viscous liquid remained behind, which crystallised from benzene and light petroleum and was found to be 3 : 4-carbonyldioxybenzylidene chloride ("dichloropiperonal"). The yield was 60 per cent. The "dichloropiperonal dichloride" of Fittig and Remsen, formed by the action of phosphorus pentachloride on piperonal, was found to distil without decomposition at 152—153°/9 mm., but could, nevertheless, not be obtained quite pure. (Found, $Cl = 50{\cdot}35$; $C_8H_4O_2Cl_4$ requires $Cl = 51{\cdot}8$ per cent.)

The impurity was probably a trace of unchanged piperonal dichloride. The tetrachloro-compound was obtained crystalline by cooling it in carbon dioxide and acetone, and was found to melt at 14—15°. It is very soluble in all organic solvents, including light petroleum. The two chlorine atoms of the methylene group are replaced by an oxygen atom through the action of anhydrous formic or acetic acid in the cold; on boiling, the second pair of chlorine atoms is removed, with the formation of Pauly's cyclic carbonate of protocatechualdehyde.

Piperonal dichloride, which was cursorily referred to by Fittig and Remsen, has now been obtained pure. When piperonal is mixed with one molecular proportion of phosphorus pentachloride, enough heat is developed to liquefy the mixture and almost complete the reaction. On distilling the phosphoryl chloride under atmospheric pressure, the residue left in the flask became dark blue and a certain amount of decomposition took place. Most of the substance, however, distilled constantly at 141°/8 mm. and at once crystallised in the receiver; the yield was 60 per cent. of the theoretical:

0·2024 gave 0·2796 AgCl. $Cl = 34{\cdot}2$.

$C_8H_6O_2Cl_2$ requires $Cl = 34{\cdot}6$ per cent.

Piperonal dichloride forms large, acicular crystals from a mixture of benzene with much light petroleum, and melts at 59°. It resembles the closely related carbonate of protocatechualdehyde dichloride ("dichloropiperonal" of Fittig and Remsen). Both substances are unstable in moist air and gradually turn blue, and both are readily converted into the corresponding aldehyde by boiling with formic acid. Piperonal dichloride was by this means reconverted into piperonal, melting at 37°

and boiling at 133°/8 mm. When piperonal is heated with an excess of thionyl chloride on the water-bath, the same dichloride is slowly formed.

The author desires to express his thanks to Mr. A. J. Ewins, B.Sc., for his valuable assistance.

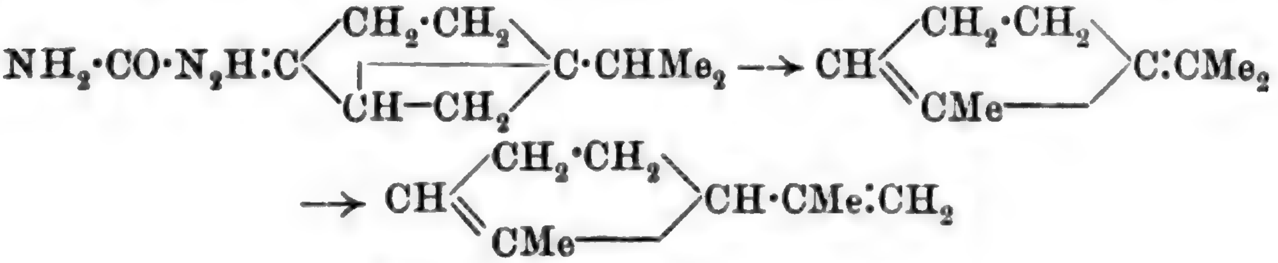
THE WELLCOME PHYSIOLOGICAL RESEARCH LABORATORIES,
HERNE HILL, LONDON, S.E.

LIII.—*Experiments on the Synthesis of the Terpenes. Part XII. Synthesis of Terpins, Terpineols, and Terpenes derived from Methyl*iso*propyl*cyclo*pentanes,* $Me{\cdot}C_5H_8{\cdot}CHMe_2$.

By WALTER NORMAN HAWORTH and WILLIAM HENRY PERKIN, jun.

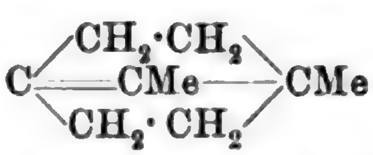
THE investigation of the naturally occurring members of the camphor and terpene series has shown that almost the whole of these substances are derived, either directly or indirectly, from one of the modifications of methyl*iso*propyl*cyclo*hexane, $Me{\cdot}C_6H_{10}{\cdot}CHMe_2$.

The terpenes derived from natural sources have the composition $C_{10}H_{16}$, and a search for lower terpenes of the composition C_9H_{14}, which might possibly be derivatives of methyl*iso*propyl*cyclo*pentane, $Me{\cdot}C_5H_8{\cdot}CHMe_2$, has disclosed only two such substances, and these are of doubtful constitution. Semmler (*Ber.*, 1902, **35**, 2047) found that sabinene ketone, when converted into the semicarbazone and then digested with 25 per cent. sulphuric acid, yields a hydrocarbon, C_9H_{14} (b. p. 165—166°). Since the molecular refraction shows that this hydrocarbon is doubly unsaturated, Semmler suggests that its formation may be assumed to take place in accordance with the scheme:



1-Methyl-2-*iso*propenyl-Δ^5-*cyclo*pentene.

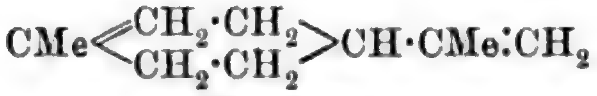
Subsequently Semmler (*Ber.*, 1904, **37**, 237) described a hydrocarbon, C_9H_{14}, of boiling point 144—146°, which he obtained from dihydrocamphoryl alcohol, $C_9H_{18}O$, by heating with anhydrous oxalic acid, but this substance evidently has the formula C_9H_{16}. The only other terpene from natural sources* which has the composition C_9H_{14}, which we have been able to find, is santene, an optically inactive hydrocarbon which was discovered by F. Müller (*Arch. Pharm.*, 1900, **238**, 366) in the low boiling fractions of sandal wood oil. This hydrocarbon distils at 139—140°, yields a blue nitroso-chloride (m. p. 108°), and a crystalline hydrochloride, C_9H_{14},HCl (m. p. 80°). Semmler (*Ber.*, 1907, **40**, 4595) subsequently showed that the molecular refraction proves that this substance contains only one double linking, and that it must, therefore, be bicyclic, and this led him to suggest the formula



as probably representing the formula of santene.

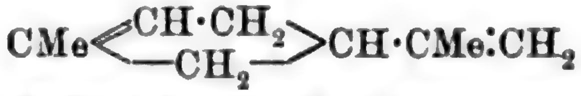
Aschan (*Ber.*, 1907, **40**, 4918) has also recently carefully investigated santene, and confirmed the composition, C_9H_{14}, the boiling point, 140°, the molecular refraction, and has also described other interesting properties of the hydrocarbon.

The consideration of these and of other facts connected with the chemistry of the terpenes led us to think that it would be interesting to attempt the synthesis of terpenes, analogously constituted to dipentene, but containing a closed ring of five-carbon atoms in the place of the six-carbon ring of that hydrocarbon,



$$\mathrm{CMe}{<}\begin{matrix}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}{>}\mathrm{CH{\cdot}CMe{:}CH_2}$$

Dipentene.

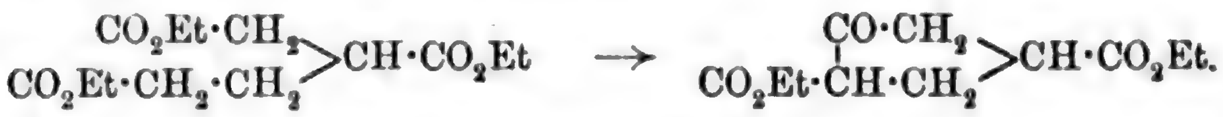


$$\mathrm{CMe}{<}\begin{matrix}\mathrm{CH{\cdot}CH_2}\\ \mathrm{—CH_2—}\end{matrix}{>}\mathrm{CH{\cdot}CMe{:}CH_2}$$

1-Methyl-3-*iso*propenyl-Δ^5-*cyclo*pentene.

and the present paper contains an account of the experiments which we have made in this direction.

A short time ago (Trans., 1906, **89**, 1641), Kay and Perkin showed that ethyl butane-$\alpha\beta\delta$-tricarboxylate reacts with sodium with the formation of ethyl *cyclo*pentanone-2 : 4-dicarboxylate, a decomposition which they formulated thus:

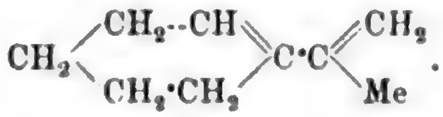


$$\begin{matrix}\mathrm{CO_2Et{\cdot}CH_2}\\ \mathrm{CO_2Et{\cdot}CH_2{\cdot}CH_2}\end{matrix}{>}\mathrm{CH{\cdot}CO_2Et} \longrightarrow \begin{matrix}\mathrm{CO{\cdot}CH_2}\\ |\\ \mathrm{CO_2Et{\cdot}CH{\cdot}CH_2}\end{matrix}{>}\mathrm{CH{\cdot}CO_2Et}.$$

The ester so produced is decomposed by boiling with dilute sulphuric

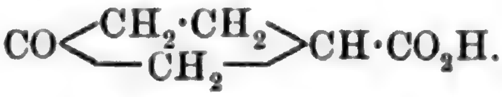
---

* A terpene, C_9H_{14}, obtained synthetically by Matsubara and Perkin (Trans., 1905, **87**, 637), is $\Delta^{3:8(9)}$-normenthadiene (b. p. 161°), and is known to contain a closed chain of six-carbon atoms and to have the constitution:



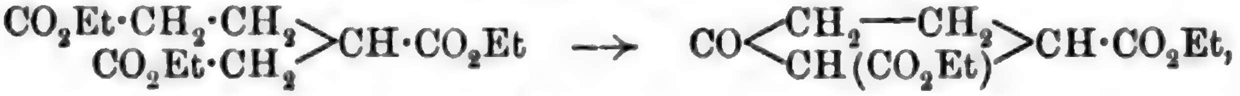
by Google

acid, with elimination of carbon dioxide and alcohol, and formation of *cyclo*pentanone-3-carboxylic acid,



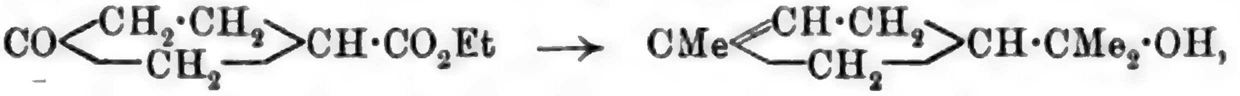
$$\mathrm{CO}{<}\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2}\end{matrix}{>}\mathrm{CH\cdot CO_2H}.$$

In continuing these experiments, we have been able to prove (p. 576) that the condensation by means of sodium takes place in a different direction from that represented above, and that the product is in reality *ethyl* cyclo*pentanone*-2 : 3-*dicarboxylate*,



$$\begin{matrix}\mathrm{CO_2Et\cdot CH_2\cdot CH_2}\\ \mathrm{CO_2Et\cdot CH_2}\end{matrix}{>}\mathrm{CH\cdot CO_2Et} \longrightarrow \mathrm{CO}{<}\begin{matrix}\mathrm{CH_2—CH_2}\\ \mathrm{CH(CO_2Et)}\end{matrix}{>}\mathrm{CH\cdot CO_2Et},$$

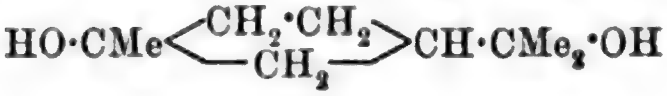
so that this view of this condensation is to be substituted for that given in the earlier paper. This change does not make any difference in regard to the constitution of the keto-acid, since the 2 : 3- and 2 : 4-dicarboxylic esters will both yield the same keto-acid on hydrolysis. We next investigated the action of magnesium methyl iodide on ethyl *cyclo*pentanone-3-carboxylate, and obtained a small quantity of 1-*methyl*-3-iso*propenol*cyclo*pentene*, which distils at 100—105° (30 mm.) and the formation of which may be represented thus:



$$\mathrm{CO}{<}\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2}\end{matrix}{>}\mathrm{CH\cdot CO_2Et} \longrightarrow \mathrm{CMe}{<}\begin{matrix}\mathrm{CH\cdot CH_2}\\ \mathrm{CH_2}\end{matrix}{>}\mathrm{CH\cdot CMe_2\cdot OH},$$

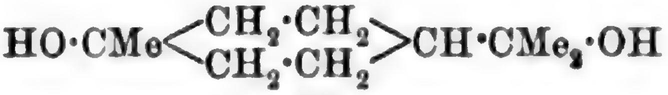
although the double linking (Δ^5) may be in the position Δ^1.

This carbinol is the terpineol of the five-carbon series, and, when shaken with dilute sulphuric acid, it is converted into the corresponding terpin, 1-*hydroxy*-1-*methyl*-3-iso*propenol*cyclo*pentane* (I),



$$\mathrm{HO\cdot CMe}{<}\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2}\end{matrix}{>}\mathrm{CH\cdot CMe_2\cdot OH}$$

(I.)

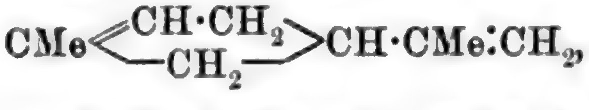


$$\mathrm{HO\cdot CMe}{<}\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{CH\cdot CMe_2\cdot OH}$$

(II.)

a crystalline substance which melts at 75°, and is especially interesting on account of its relationship to ordinary terpin (II).

Lastly, a small quantity of a hydrocarbon, 1-*methyl*-3-iso*propenyl*-cyclo*pentene*, is produced during the action of magnesium methyl iodide on ethyl *cyclo*pentanone-3-carboxylate, which distils at about 150°, and is the representative of dipentene in the pentane series. It is probable that its constitution is represented by the formula

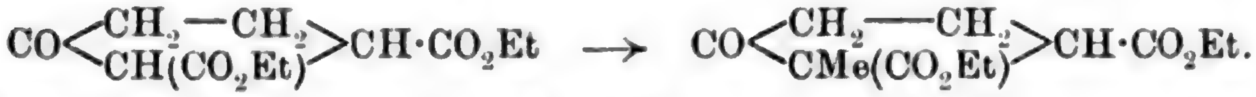


$$\mathrm{CMe}{<}\begin{matrix}\mathrm{CH\cdot CH_2}\\ \mathrm{CH_2}\end{matrix}{>}\mathrm{CH\cdot CMe{:}CH_2},$$

but the position of the double linking in the ring is doubtful.

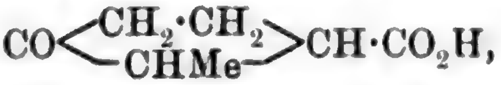
A second series of experiments, designed with the object of synthesising other terpins, terpineols, and terpenes of the pentane series, was carried out in the following manner.

The sodium derivative of ethyl *cyclo*pentanone-2 : 3-dicarboxylate was digested with methyl iodide, and thus converted into *ethyl-2-methyl*cyclo*pentanone-2* : 3-*dicarboxylate*,



$$\mathrm{CO}\left<\begin{matrix}\mathrm{CH_2{-}CH_2}\\\mathrm{CH(CO_2Et)}\end{matrix}\right>\mathrm{CH\cdot CO_2Et} \longrightarrow \mathrm{CO}\left<\begin{matrix}\mathrm{CH_2{-}CH_2}\\\mathrm{CMe(CO_2Et)}\end{matrix}\right>\mathrm{CH\cdot CO_2Et}.$$

When this ester is hydrolysed by dilute hydrochloric acid, it yields a small quantity of 2-*methyl*cyclo*pentanone*-3-*carboxylic acid* (m. p. 95°),



$$\mathrm{CO}\left<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\\mathrm{CHMe}\end{matrix}\right>\mathrm{CH\cdot CO_2H},$$

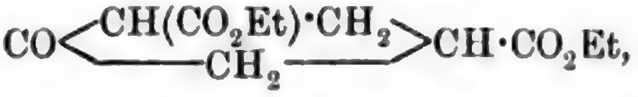
but by far the larger proportion of the ester is further hydrolysed with the formation of *pentane-βγε-tricarboxylic acid* (m. p. 177°),

$$\mathrm{CO_2H\cdot CHMe\cdot CH(CO_2H)\cdot CH_2\cdot CH_2\cdot CO_2H}.$$

In order to prove the constitution of the latter acid, it was prepared synthetically by digesting the sodium derivative of ethyl cyano-β-methylsuccinate with ethyl β-iodopropionate and subsequently hydrolysing the resulting *ethyl γ-cyanopentane-βγε-tricarboxylate* with concentrated hydrochloric acid:

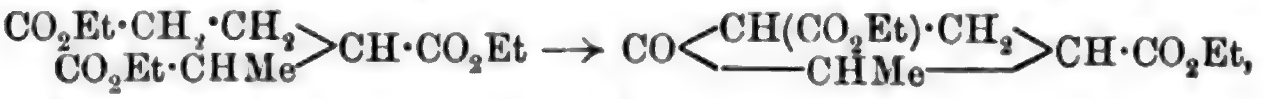
$$\mathrm{CO_2Et\cdot CHMe\cdot CNa(CN)\cdot CO_2Et + CH_2I\cdot CH_2\cdot CO_2Et} \longrightarrow$$
$$\mathrm{CO_2Et\cdot CHMe\cdot C(CN)(CO_2Et)\cdot CH_2\cdot CH_2\cdot CO_2Et} \longrightarrow$$
$$\mathrm{CO_2H\cdot CHMe\cdot CH(CO_2H)\cdot CH_2\cdot CH_2\cdot CO_2H}.$$

The acid thus synthesised melted at 177°, and was identical with that obtained by the hydrolysis of ethyl 2-methyl*cyclo*pentanone-2 : 3-dicarboxylate, and this fact clearly proves that the product of the action of sodium on ethyl butane-αβδ-tricarboxylate (Kay and Perkin, *loc. cit.*) must be ethyl *cyclo*pentanone-2 : 3-dicarboxylate, and cannot be ethyl *cyclo*pentanone-2 : 4-dicarboxylate,



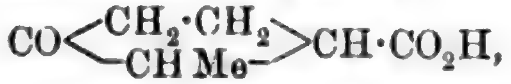
$$\mathrm{CO}\left<\begin{matrix}\mathrm{CH(CO_2Et)\cdot CH_2}\\\mathrm{CH_2}\end{matrix}\right>\mathrm{CH\cdot CO_2Et},$$

as was first thought to be the case, since the latter ester, after methylation, could not yield pentane-βγε-tricarboxylic acid as the product of hydrolysis. When ethyl pentane-βγε-tricarboxylate is treated with sodium, it readily undergoes internal condensation with the formation of *ethyl* 2-*methyl*cyclo*pentanone*-3 : 5-*dicarboxylate*,



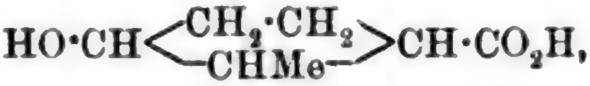
$$\begin{matrix}\mathrm{CO_2Et\cdot CH_2\cdot CH_2}\\\mathrm{CO_2Et\cdot CHMe}\end{matrix}\!\!>\mathrm{CH\cdot CO_2Et} \longrightarrow \mathrm{CO}\left<\begin{matrix}\mathrm{CH(CO_2Et)\cdot CH_2}\\\mathrm{CHMe}\end{matrix}\right>\mathrm{CH\cdot CO_2Et},$$

and this ester, on hydrolysis with hydrochloric acid, yields 2-methyl*cyclo*pentanone-3-carboxylic acid (m. p. 95°),

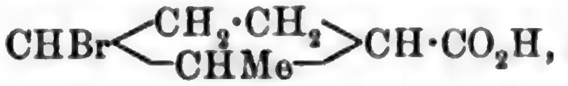


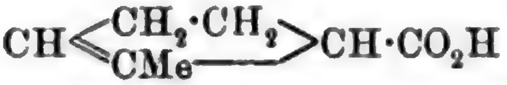
$$\mathrm{CO}\left<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\\mathrm{CHMe}\end{matrix}\right>\mathrm{CH\cdot CO_2H},$$

of which mention has already been made, and, indeed, nearly all of this keto-acid which we required in such large quantities for this research was made in this way. When the keto-acid is reduced with sodium amalgam, it is converted into 2-*methyl*cyclo*pentanol-3-carboxylic acid*,



$$\mathrm{HO{\cdot}CH}\left\langle\begin{matrix}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CHMe}\end{matrix}\right\rangle\mathrm{CH{\cdot}CO_2H},$$

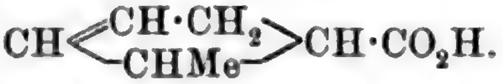
which, although it is a γ-hydroxy-acid, distils at 182—185° (20 mm.) without conversion into the lactone, a fact which is possibly due to the acid, so obtained, being the *trans*-modification. It reacts readily with hydrobromic acid, and is converted into 5-*bromo*-1-*methyl*-cyclo*pentane*-2-*carboxylic acid*,  $\mathrm{CHBr}\left\langle\begin{matrix}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CHMe}\end{matrix}\right\rangle\mathrm{CH{\cdot}CO_2H}$, and the ethyl ester of this acid is decomposed by boiling diethylaniline with formation of an oil which was ultimately shown to be a mixture of the esters of the two possible unsaturated acids,



$$\mathrm{CH}\left\langle\!\!\left\langle\begin{matrix}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CMe}\end{matrix}\right.\right.\!\!\left.\right\rangle\mathrm{CH{\cdot}CO_2H}$$

1-*Methyl*-Δ^5-cyclo*pentene*-
2-*carboxylic acid*.

and



$$\mathrm{CH}\left\langle\begin{matrix}\mathrm{CH{\cdot}CH_2}\\ \mathrm{CHMe}\end{matrix}\right\rangle\mathrm{CH{\cdot}CO_2H}.$$

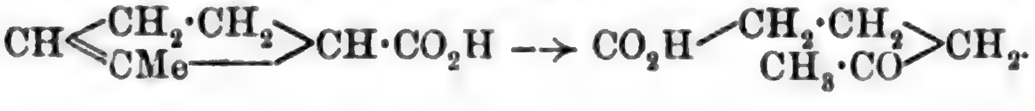
1-*Methyl*-Δ^4-cyclo*pentene*-
2-*carboxylic acid*.

The oily mixture of acids obtained when the ester is hydrolysed could not be separated into the constituents by the fractional crystallisation of such salts as we prepared, and for a long time there seemed to be little prospect of effecting the separation.

Subsequently, the remarkable fact was discovered that the difference in the rate of esterification of the two isomerides and also in the rate of hydrolysis of the esters is so great that a complete separation can be based on this behaviour.

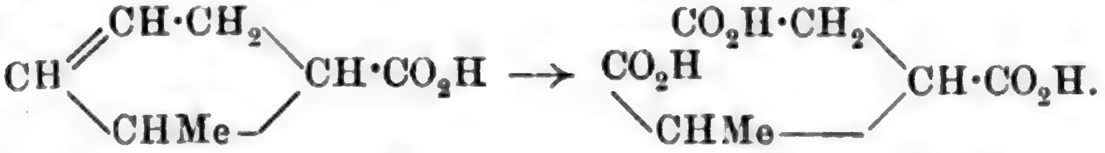
The Δ^4-acid esterifies in contact with alcohol and sulphuric acid at the ordinary temperature in a few hours, whereas the esterification of the Δ^5-acid is not complete after four days, and again the ester of the Δ^4-acid is hydrolysed by methyl-alcoholic potash in the cold in a few hours, whereas, under the same conditions, hydrolysis of the ester of the Δ^5-acid is not complete in five days. This difference in behaviour made it possible to work out a complete separation of the two acids, and the details of the method are explained on p. 585. The two acids are strikingly different in their physical properties. One of them is a solid, melts at 131°, and possesses a quite unusual facility in crystallising from solvents; the other is a liquid, distils at 165° (100 mm.), and shows no sign of crystallising when it is cooled in a freezing mixture.

The next step was to determine the constitutions of these acids, and this was done in each case by oxidising with ozone in alkaline solution. In these circumstances, the acid melting at 131° yielded γ-*acetobutyric acid*; it must therefore be 1-*methyl*-Δ^5-cyclo*pentene*-2-*carboxylic acid*,

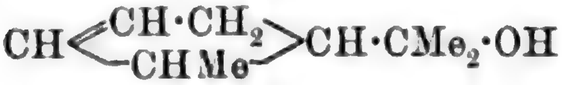


$$\mathrm{CH}\left\langle\!\!\left\langle\begin{matrix}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CMe}\end{matrix}\right.\right.\!\!\left.\right\rangle\mathrm{CH{\cdot}CO_2H}\longrightarrow\mathrm{CO_2H}\diagup\begin{matrix}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CH_3{\cdot}CO}\end{matrix}\Big\rangle\mathrm{CH_2}.$$

The liquid acid is converted by oxidation, first with ozone and then with chromic acid, into *a-methyltricarballylic acid*, a behaviour which clearly proves that it is 1-*methyl*-Δ^4-cyclo*pentene*-2-*carboxylic acid*,

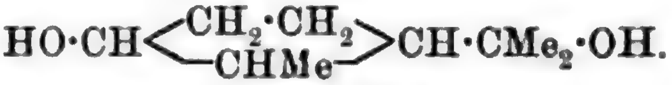


The next step was the investigation of the action of magnesium methyl iodide on the ester of the Δ^4-acid, a process which resulted in the formation of an almost quantitative yield of 1-*methyl*-2-iso*propenol*-Δ^4-cyclo*pentene* (I):



$\mathrm{CH}{<}\genfrac{}{}{0pt}{}{\mathrm{CH\cdot CH_2}}{\mathrm{CHMe}}{>}\mathrm{CH\cdot CMe_2\cdot OH}$

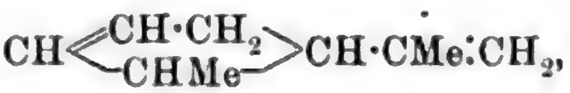
(I.)



$\mathrm{HO\cdot CH}{<}\genfrac{}{}{0pt}{}{\mathrm{CH_2\cdot CH_2}}{\mathrm{CHMe}}{>}\mathrm{CH\cdot CMe_2\cdot OH.}$

(II.)

This interesting substance distils at 95° (30 mm.), and resembles terpineol in odour and in the fact that, when shaken with dilute sulphuric acid, it yields the corresponding terpin, namely, 5-*hydroxy*-1-*methyl*-2-iso*propenol*cyclo*pentane*, which crystallises well, melts at 72°, and probably has the constitution (II), but the hydroxyl group in the ring may obviously be situated in the position 4. In one respect in particular, the carbinol differs in a striking way from terpineol. It is well known that terpineol is readily and almost quantitatively converted into dipentene when it is heated with dehydrating agents, but the most unexpected difficulties were encountered in attempting the analogous elimination of water from the carbinol. Ultimately we were able, by employing succinic anhydride as the dehydrating agent, to obtain a small quantity of 1-*methyl*-2-iso*propenyl*-Δ^4-cyclo*pentene*,

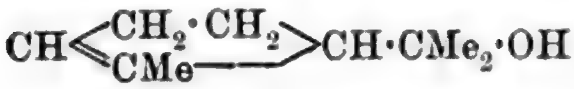


$\mathrm{CH}{<}\genfrac{}{}{0pt}{}{\mathrm{CH\cdot CH_2}}{\mathrm{CHMe}}{>}\mathrm{CH\cdot CMe{:}CH_2},$

and this interesting hydrocarbon was found to distil at 143—145° (770 mm.), and to have an odour closely resembling that of dipentene.

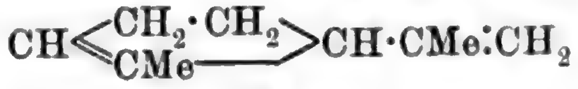
When other dehydrating agents were employed, the product consisted almost entirely of polymerised hydrocarbons, one of which distilled at 170—175° (20 mm.), and evidently had the constitution $(C_9H_{14})_2$.

The first example of this kind of polymerisation was met with during the investigation of the action of potassium hydrogen sulphate on Δ^3-normenthenol(8) (Matsubara and Perkin, Trans., 1905, 87, 668), when only a small quantity of $\Delta^{3:8(9)}$-normenthadiene, C_9H_{14}, was formed, and the product consisted principally of dinormenthadiene, $(C_9H_{14})_2$, which distilled at 170—172° (16 mm.), or at practically the same temperature as the polymeride mentioned above. Still greater difficulties were met with in investigating the action of magnesium methyl iodide on the ester of 1-methyl-Δ^5-*cyclo*pentene-2-carboxylic acid, as in this case only a very small quantity of 1-*methyl*-2-iso*propenol*-Δ^5-cyclo*pentene* (I) is formed, and the product consists



$$\mathrm{CH}\Big\langle\begin{matrix}\mathrm{CH_2\cdot CH_2}\\\mathrm{CMe}\text{———}\end{matrix}\Big\rangle\mathrm{CH\cdot CMe_2\cdot OH}$$

(I.)



$$\mathrm{CH}\Big\langle\begin{matrix}\mathrm{CH_2\cdot CH_2}\\\mathrm{CMe}\text{———}\end{matrix}\Big\rangle\mathrm{CH\cdot CMe{:}CH_2}$$

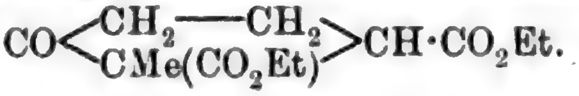
(II.)

almost entirely of a polymerised terpene, $(C_9H_{14})_2$, and of other higher condensation products.

It is unfortunate that it was not found possible to obtain 1-*methyl*-2-iso*propenyl*-Δ^5-cyclo*pentene* (II) in sufficient quantity for characterisation, since this terpene has the constitution which Semmler (*loc. cit.*) suggested for the hydrocarbon which he obtained from sabinene ketone (p. 573).

EXPERIMENTAL.

Ethyl 2-*Methyl*cyclo*pentanone*-2 : 3-*dicarboxylate*,



$$\mathrm{CO}\Big\langle\begin{matrix}\mathrm{CH_2}\text{——}\mathrm{CH_2}\\\mathrm{CMe(CO_2Et)}\end{matrix}\Big\rangle\mathrm{CH\cdot CO_2Et.}$$

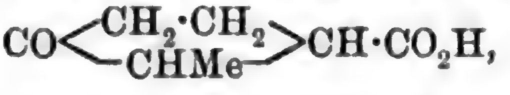
In order to prepare this ester, sodium (23 grams) was dissolved in ethyl alcohol (300 c.c.) and, after cooling, 228 grams of ethyl *cyclo*pentanone-2 : 3-dicarboxylate (Kay and Perkin, Trans., 1906, **89**, 1640) were carefully added, the flask being cooled during the addition.

The deep yellow solution was mixed with methyl iodide (150 grams), when little evolution of heat occurred at first, but, on standing, the mixture soon became warm, and gradually the temperature rose to the boiling point. After remaining for two hours, the reaction was completed by heating on the water-bath for an hour, water was then added, and the oily ester extracted with ether. The ethereal solution was well washed, dried over calcium chloride, and evaporated, when a small quantity of the oil was distilled and found to boil at about 170° (18 mm.):

0·1802 gave 0·3915 CO_2 and 0·1232 H_2O. C = 59·2 ; H = 7·6.

$C_{12}H_{18}O_5$ requires C = 59·5 ; H = 7·4 per cent.

Hydrolysis of Ethyl 2-*Methyl*cyclo*pentanone*-2 : 3-*dicarboxylate*. *Formation of* 2-*Methyl*cyclo*pentanone*-3-*carboxylic Acid*,



$$\mathrm{CO}\Big\langle\begin{matrix}\mathrm{CH_2\cdot CH_2}\\\mathrm{CHMe}\text{——}\end{matrix}\Big\rangle\mathrm{CH\cdot CO_2H,}$$

and Pentane-$\beta\gamma\epsilon$-*tricarboxylic Acid*,

$CO_2H\cdot CHMe\cdot CH(CO_2H)\cdot CH_2\cdot CH_2\cdot CO_2H$.

The curious behaviour of ethyl 2-methyl*cyclo*pentanone-2 : 3-dicarboxylate, on hydrolysis with hydrochloric acid, has been discussed in the introduction (p. 576), and the following experiment has often been repeated and always with the same results. The ester was mixed with three times its volume of dilute hydrochloric acid (1 vol. conc. HCl and 9 vols. of water), and digested in a reflux apparatus for eight hours. When the oil had completely dissolved, the air condenser was removed, from time to time, in order to allow the alcohol to escape; the solution was saturated with ammonium sulphate, and extracted with pure ether, five times by hand and ten times on the shaking machine.* The ethereal extract was dried over calcium chloride and evaporated, and the residual viscid oil, which consisted of a mixture of methyl*cyclo*pentanonecarboxylic acid and pentane-$\beta\gamma\epsilon$-tricarboxylic acid, was esterified by digesting with a 10 per cent. solution of sulphuric acid in alcohol for fifteen hours. The product was mixed with much ether, water was added, and the ethereal layer, after washing with water and dilute sodium carbonate and drying over calcium chloride, was evaporated, and the residual oil fractionated under 20 mm. pressure, when it was somewhat readily separated into two portions distilling at 130—135° and 180—185° respectively.

The lower fraction consists of *ethyl 2-methyl*cyclo*pentanone-3-carboxylate*:

0·1310 gave 0·3010 CO_2 and 0·0988 H_2O. C = 62·7; H = 8·4.

$C_9H_{14}O_3$ requires C = 63·5; H = 8·2 per cent.

This ester, when hydrolysed with dilute hydrochloric acid, yields 2-*methyl*cyclo*pentanone-3-carboxylic acid*, which melts at 95°, and the preparation and properties of which are described on p. 582.

The higher fraction is *ethyl pentane-$\beta\gamma\epsilon$-tricarboxylate*:

0·1279 gave 0·2748 CO_2 and 0·0967 H_2O. C = 58·6; H = 8·4.

$C_{14}H_{24}O_6$ requires C = 58·3; H = 8·3 per cent.

A small quantity of this ester was digested with hydrochloric acid for six hours and evaporated to dryness, when a syrup remained which gradually crystallised. The mass was well stirred with a little concentrated hydrochloric acid, transferred to porous porcelain, and the almost colourless residue crystallised from hydrochloric acid, from which the new acid separated as a colourless, sandy powder and melted at 177°:

0·1294 gave 0·2224 CO_2 and 0·0710 H_2O. C = 46·9; H = 6·1.

$C_8H_{12}O_6$ requires C = 47·1; H = 5·9 per cent.

That this acid is tribasic was shown by titration with decinormal sodium hydroxide, when 0·1220 required 0·0713 NaOH for neutralisation, whereas this amount of a tribasic acid, $C_8H_{12}O_6$, should neutralise 0·0719 NaOH.

---

* The last three extractions yielded a syrupy acid, which crystallised on standing and proved to be almost pure pentane-$\beta\gamma\epsilon$-tricarboxylic acid.

Synthesis of Pentane-βγε-tricarboxylic Acid, $CO_2H·CHMe·CH(CO_2H)·CH_2·CH_2·CO_2H$, *from Ethyl Cyano-β-methylsuccinate.*

This synthesis was carried out in order to prove that the acid of melting point 177°, obtained as explained in the previous section, is pentane-βγε-tricarboxylic acid, and also because it was found to be the best method for the preparation of the large quantities of this acid required for this research.

Ethyl cyano-β-methylsuccinate, $CO_2Et·CH(CN)·CHMe·CO_2Et$ (35·5 grams), prepared from the sodium derivative of ethyl cyanoacetate and ethyl α-bromopropionate by the method recommended by Bone and Sprankling (Trans., 1899, **75**, 853), was converted into the sodium derivative by the addition of sodium (3·9 grams) dissolved in alcohol (60 c.c.) and mixed with ethyl β-iodopropionate (38 grams), the whole being kept as cold as possible during the addition. After remaining overnight, the product was heated on the water-bath for half an hour, mixed with water, extracted with ether, and, after washing with water and drying over calcium chloride, the ether was evaporated and the residual oil fractionated under reduced pressure, when an almost quantitative yield of *ethyl γ-cyanopentane-βγε-tricarboxylate* was obtained as a colourless oil distilling at 212° (25 mm.):

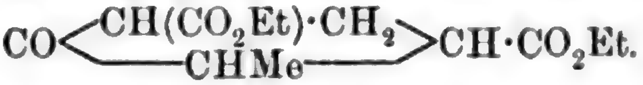
0·2060 gave 8·4 c.c. nitrogen at 14° and 752 mm. N = 4·7.
$C_{15}H_{23}O_6N$ requires N = 4·5 per cent.

The cyano-ester was hydrolysed by digesting in a reflux apparatus with three times its volume of concentrated hydrochloric acid for twenty hours, the condenser being removed every couple of hours for a few minutes in order to allow the alcohol to escape. The clear solution was evaporated to dryness, and the solid residue of acid and ammonium chloride crystallised several times from concentrated hydrochloric acid, from which the *pentane-βγε-tricarboxylic acid* separates as a colourless, sandy powder melting at 177°:

0·1247 gave 0·2137 CO_2 and 0·0685 H_2O. C = 46·8; H = 6·1.
$C_8H_{12}O_6$ requires C = 47·1; H = 5·9 per cent.

That this acid was identical with the tribasic acid, $C_8H_{12}O_6$, obtained as described on page 580, was proved by the fact that a mixture of the two specimens melted at 176—177°.

*Ethyl 2-Methyl*cyclo*pentanone-3 : 5-dicarboxylate*,



$$\mathrm{CO}<\begin{matrix}\mathrm{CH(CO_2Et)\cdot CH_2}\\ \mathrm{CHMe}\end{matrix}>\mathrm{CH\cdot CO_2Et}.$$

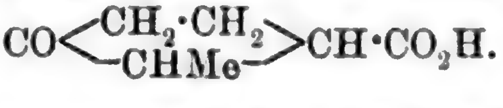
The sodium derivative of this ketonic ester is readily formed when sodium reacts with ethyl pentane-βγε-tricarboxylate under the following conditions. Sodium (23 grams) is melted under boiling toluene, and vigorously shaken in order to bring it into as fine a state of division as possible, the toluene is poured off, the sodium powder washed with benzene by decantation, and then mixed with ethyl pentanetricarboxylate (144 grams) dissolved in about 150 grams of pure dry benzene. A long air condenser is attached to the flask, and the mixture gently warmed on the water-bath until a brisk reaction sets in, the flask is then removed from the water-bath, and the reaction allowed to proceed without further external heating, and, indeed, it is sometimes necessary to cool the flask. After about half an hour, the product is heated on the water-bath until the sodium has completely disappeared, an operation which requires usually two and a-half hours. The brown mass is mixed with ether, the sodium derivative decomposed by ice and dilute hydrochloric acid, and the ethereal solution separated. The aqueous solution is twice extracted with ether, the combined ethereal extracts are then well washed with dilute sodium carbonate, which removes much colouring matter,* and dried over calcium chloride. After distilling off the ether and fractionating under reduced pressure, almost the whole quantity passes over at about 180° (25 mm.), and consists of pure *ethyl 2-methyl*cyclo*pentanone-3 : 5-dicarboxylate*, the yield being about 70 per cent. of that theoretically possible:

0·2000 gave 0·4346 CO_2 and 0·1368 H_2O. C = 59·3 ; H = 7·6.

$C_{12}H_{18}O_5$ requires C = 59·5 ; H = 7·4 per cent.

This ester is a colourless oil, the alcoholic solution of which gives a violet coloration on the addition of ferric chloride.

*2-Methyl*cyclo*pentanone-3-carboxylic Acid*,



$$\mathrm{CO}<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CHMe}\end{matrix}>\mathrm{CH\cdot CO_2H}.$$

The considerable quantities of this keto-acid which were required for this research were prepared either by the hydrolysis of ethyl

---

* If the dark-coloured extract is acidified with dilute hydrochloric acid and boiled for 5 hours, a considerable quantity of crude 2-methyl*cyclo*pentanone-3-carboxylic acid may be obtained by extraction with ether. It is best purified by conversion into its ester, and, after fractionating this, hydrolysing with dilute hydrochloric acid.

2-methyl*cyclo*pentanone-2 : 3-dicarboxylate (p. 579) or of ethyl 2-methyl*cyclo*pentanone-3 : 5-dicarboxylate (see previous section).

In either case, the ester was digested in a reflux apparatus with four times its volume of 10 per cent. hydrochloric acid until solution was complete, the condenser being removed from time to time in order to allow the alcohol produced to escape. The clear solution was saturated with ammonium sulphate and extracted several times with pure ether, the ethereal solution was dried over calcium chloride, evaporated, and the residue fractionated under reduced pressure, when almost the whole quantity distilled at 190—193° (20 mm.) and crystallised on cooling. The crystalline mass was left in contact with porous porcelain until quite free from oil and then crystallised from ether, in which it is readily soluble, but from the concentrated solution in which it separates in hard, nodular masses :

0·1296 gave 0·2826 CO_2 and 0·0850 H_2O. C = 59·4 ; H = 7·2.
0·1431 „ 0·3091 CO_2 „ 0·0935 H_2O. C = 58·9 ; H = 7·2.
$C_7H_{10}O_3$ requires C = 59·1 ; H = 7·1 per cent.

2-*Methyl*cyclo*pentanone-3-carboxylic acid* melts at 95°, and is very readily soluble in water and most organic solvents ; it is very sparingly soluble in cold light petroleum, but dissolves readily on warming and separates, when the solution is allowed to cool slowly, as a glistening, satiny mass.

The *semicarbazone* was prepared by adding semicarbazide hydrochloride and sodium acetate to a hot moderately dilute solution of the acid in water. On standing, the clear liquid gradually deposited a mass of crystals, which were collected and crystallised from water, when the semicarbazone was obtained as a sandy powder which decomposes at about 200—202° :

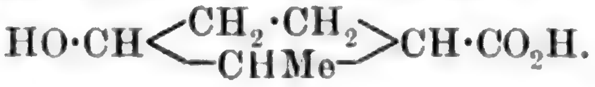
0·1010 gave 17·6 c.c. nitrogen at 14° and 766 mm. N = 20·6.
$C_8H_{13}O_3N_3$ requires N = 21·2 per cent.

The *Oxime.*—In order to prepare this derivative, the pure acid (2 grams) was dissolved in water, mixed with hydroxylamine hydrochloride (2 grams) and potassium hydroxide (4 grams), and allowed to stand for twelve hours. The solution was acidified, extracted with much ether, the ethereal solution dried over calcium chloride, and evaporated, when a syrup was obtained which soon crystallised. The product was drained on porous porcelain and crystallised from ether, from which the oxime separates in crusts, which soften at 140° and melt at about 155° with gradual decomposition ; at 160°, the substance very rapidly becomes dark brown :

0·1963 gave 15·6 c.c. nitrogen at 18° and 762 mm. N = 9·1.
$C_7H_{11}O_3N$ requires N = 8·9 per cent.

This oxime is readily soluble in water or alcohol, but sparingly so in dry ether, chloroform, or benzene.

2-*Methylcyclopentanol-3-carboxylic Acid*,



$$HO\cdot CH<\begin{matrix}CH_2\cdot CH_2\\ CHMe\end{matrix}>CH\cdot CO_2H.$$

The reduction of 2-methyl*cyclo*pentanone-3-carboxylic acid was carried out by treating the solution of the acid (30 grams) in sodium carbonate with 1·5 kilos. of freshly-prepared[*] sodium amalgam in a bottle fitted with a mechanical stirrer, hydrochloric acid being added from time to time in such a way that the liquid remained always slightly alkaline. The product was acidified with hydrochloric acid, saturated with ammonium sulphate, and extracted at least twelve times with ether on the machine. The first three extractions contained always a small quantity of unchanged keto-acid, and this portion was submitted to further reduction; the other extracts were dried over calcium chloride, evaporated, and the viscid syrup distilled under reduced pressure, when the pure hydroxy-acid passed over at 182—185° (20 mm.):

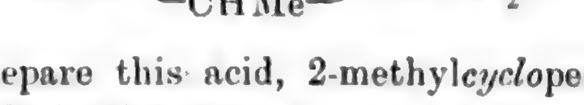
0·1800 gave 0·3874 CO_2 and 0·1316 H_2O. $C = 58·7$; $H = 8·1$.

$C_7H_{12}O_3$ requires $C = 58·3$; $H = 8·3$ per cent.

This analysis shows conclusively that, although the substance is a γ-hydroxy-acid, no lactone formation had taken place during distillation; it is therefore probable that the acid prepared by the method described above is the *trans*-modification.

2-*Methylcyclopentanol-3-carboxylic acid* is a very viscid syrup, which, directly after distillation, sometimes had a pale chartreuse-green colour; it is readily soluble in water.

5-*Bromo*-1-*methylcyclopentane*-2-*carboxylic Acid*,



$$CHBr<\begin{matrix}CH_2\cdot CH_2\\ CHMe\end{matrix}>CH\cdot CO_2H.$$

In order to prepare this acid, 2-methyl*cyclo*pentanol-3-carboxylic acid is mixed in a flask with three times its volume of aqueous hydrobromic acid (saturated at 0°), and heated on the water-bath for half an hour. The product will have separated into two layers, the upper one, consisting of the bromo-acid, is often dark brown while hot, and becomes dark blue on cooling. After adding water, the heavy oil is extracted with ether, the ethereal solution well washed with water, dried over calcium chloride, and evaporated, when an oil remains which always contains some unsaturated acid produced by elimination of hydrogen bromide. A specimen which had remained for some hours in an evacuated desiccator over sulphuric acid gave the following results on analysis:

---

[*] The sodium amalgam used in these experiments was always prepared from freshly distilled mercury and carefully cleaned sodium because, if this precaution is not observed, the reduction of the keto-acid is always very slow and incomplete.

0·4131 gave 0·3195 AgBr. Br = 33·0.

$C_7H_{11}O_2Br$ requires Br = 38·6 per cent.

It sometimes happens during the preparation of the bromo-acid that a quantity of crystals separate when the product of the reaction is allowed to remain overnight. These were collected and recrystallised from formic acid, when beautiful, feathery crystals were obtained, which melted at 130—131°, and were found to consist of pure 1-methyl-Δ^5-*cyclo*pentene-2-carboxylic acid (see p. 586).

*Ethyl Bromomethyl*cyclo*pentanecarboxylate.*—This ester was prepared by digesting the crude bromo-acid with alcohol containing 10 per cent. of sulphuric acid for six hours on the water-bath. Water was then added, the oily ester extracted with ether, the ethereal solution washed with dilute sodium carbonate, dried over calcium chloride, evaporated, and the ester fractionated under reduced pressure, when it distilled at 160—165° (100 mm.) and at about 145° (50 mm.).

Owing to the presence of unsaturated esters (see next section), analysis always gave a percentage of bromine considerably lower than that theoretically required.

Formation and Separation of 1-*Methyl*-Δ^4-cyclo*pentene-2-carboxylic Acid and* 1-*Methyl*-Δ^5-cyclo*pentene-2-carboxylic Acid.*

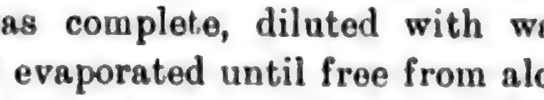
The esters of these unsaturated acids are produced when ethyl 5-bromo-1-methyl*cyclo*pentane-2-carboxylate (see the last section) is digested with diethylaniline. The fraction of the crude bromo-ester distilling at 160—170° (100 mm.) was gently boiled with three times its volume of pure diethylaniline for two hours, when the elimination of hydrogen bromide proceeded smoothly and with very little darkening. The product was mixed with much ether, the ethereal solution repeatedly extracted with dilute hydrochloric acid, dried over calcium chloride and evaporated, and the residual oil fractionated under reduced pressure, when almost the whole quantity passed over at 120—130° (100 mm.). This pungent and very unpleasant smelling oil is a mixture of the esters of the two acids mentioned at the head of this section, and the separation of these acids was accomplished (as explained in the introduction) by taking advantage of the fact that the ester of 1-methyl-Δ^4-*cyclo*pentenecarboxylic acid is much more readily formed and hydrolysed than that of the 1-methyl-Δ^5-*cyclo*-

pentenecarboxylic acid. The separation was readily carried out under the following conditions.

The esters (52 grams) were mixed with a cold solution of potassium hydroxide (30 grams) in methyl alcohol, when it was noticed that the temperature rose slightly, but care was taken that it did not rise at any time above 20°. After remaining overnight, the product was diluted with water, the unchanged ester of the Δ^5-acid extracted with ether, and the aqueous solution acidified, when an oily acid separated which was extracted with ether. After drying over calcium chloride and evaporating, the oily acid was dissolved in methyl alcohol (200 c.c.) and sulphuric acid (10 c.c.) in the cold, and allowed to remain for twelve hours. Water was then added, the oily ester extracted with ether, and the ethereal extract well agitated with dilute sodium carbonate, when, on acidifying the aqueous extract, about 4 grams of the Δ^5-acid separated at once in a crystalline and almost pure condition. This process of esterification and hydrolysis was repeated five times, and after the third time it was observed that the acid esterified readily and completely, and that the sodium carbonate extract did not yield any solid acid on acidification.

The oil from the fifth esterification distils constantly at 120—122° (100 mm.), and is pure *ethyl* 1-*methyl*-Δ^4-cyclo*pentene*-2-*carboxylate* (p. 589).

1-*Methyl*-Δ^5-cyclo*pentene*-2-*carboxylic Acid*,



$$\mathrm{CH}\Big\langle\begin{array}{c}\mathrm{CH_2\cdot CH_2}\\ \mathrm{—CMe—}\end{array}\Big\rangle\mathrm{CH\cdot CO_2H.}$$

During the process of separation from the Δ^4-acid by esterification (see the previous section), this acid was obtained partly as the free acid and partly in the form of its ester. The ester was left in contact with a large excess of methyl-alcoholic potash for several days and until hydrolysis was complete, diluted with water, saturated with carbon dioxide, and evaporated until free from alcohol.

When the cold product was acidified with hydrochloric acid, the Δ^5-acid separated at once in a crystalline condition. In order to purify the crude acid, it is dissolved in sodium carbonate, digested with animal charcoal, and, after filtering and acidifying, the colourless precipitate is collected and crystallised either from ether or light petroleum:

0·1196 gave 0·2932 CO_2 and 0·0870 H_2O. C = 66·8; H = 8·1.

$C_7H_{10}O_2$ requires C = 66·7; H = 7·9 per cent.

1-*Methyl*-Δ^5-cyclo*pentene*-2-*carboxylic acid* melts at 130—131°, and is readily soluble in ether, alcohol, or hot light petroleum, but sparingly so in water or formic acid in the cold. When its ethereal solution is allowed to evaporate very slowly, it separates in large, striated, four-sided plates or prisms with bevelled edges, twin crystals being frequent. It is readily soluble in warm formic acid (D 1·20), and crystallises well from this solvent in long, striated plates. The most convenient solvent for recrystallisation is, however, light petroleum (b. p. 100—110°), from which it separates in needles radiating from a point. The solution of the acid in dilute sodium carbonate rapidly decolorises permanganate, and the chloroform solution readily decolorises bromine (see below). It dissolves in concentrated sulphuric acid to a colourless solution, but, when warmed, this rapidly becomes dark reddish-brown, and sulphur dioxide is produced in quantity. The finely-powdered acid dissolves in much hydrobromic acid (saturated at 0°), but without the formation of an additive product, since the solution, especially when exposed to air, deposits crystals of the unchanged acid. This behaviour is unusual, because acids of this kind usually combine with great readiness with hydrobromic acid. The double linking in this methyl*cyclo*pentenecarboxylic acid is in the 1 : 5-position, and it was thought possible that intramolecular change to the 1 : 2-position might take place on boiling with alkalis, but this does not appear to be the case, since, after digesting with potash, of density 1·3, for ten minutes, the acid was recovered unchanged on the addition of hydrochloric acid.

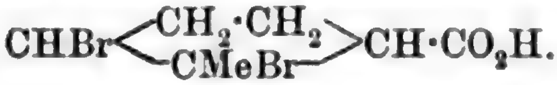
Ethyl Methyl-Δ^5-cyclo*pentenecarboxylate.*—This ester was prepared by digesting the pure acid (12 grams) with alcohol (100 c.c.) and sulphuric acid (3 c.c.) for three hours, and, after remaining overnight, the product was dissolved in ether, mixed with water, the ethereal solution thoroughly washed with water and dilute sodium carbonate, dried over calcium chloride, evaporated, and the residual oil fractionated under reduced pressure:

0·1378 gave 0·3530 CO_2 and 0·1164 H_2O. $C = 69·9$; $H = 9·1$.

$C_9H_{14}O_2$ requires $C = 70·1$; $H = 9·1$ per cent.

The ester distils constantly at 133° (100 mm.), and has a penetrating, unpleasant, and very persistent odour, which closely resembles, but is perhaps not quite so pungent as, that of the ester of the Δ^4-acid (p. 589).

1 : 5-*Dibromo-*1-*methyl*cyclo*pentane-*2-*carboxylic Acid,*



$$CHBr\Big\langle\begin{matrix}CH_2\cdot CH_2\\ CMeBr\end{matrix}\Big\rangle CH\cdot CO_2H.$$

In order to prepare this dibromo-acid, methyl-Δ^5-*cyclo*pentenecarboxylic acid (0·5 gram) was dissolved in chloroform (10 c.c.), cooled in ice, and bromine added drop by drop, when the colour disappeared rapidly at first, but remained when 0·63 gram had been added.

The end point was, however, not very sharp, and a trace of hydrogen bromide was formed. The amount of acid taken requires 0·64 gram of bromine to form the dibromo-additive product. The solution was poured on a clock glass and left exposed to air until the chloroform had evaporated; the solid residue was then recrystallised from light petroleum (b. p. 70—80°):

0·221 gave 0·2922 AgBr. Br = 56·2.

$C_7H_{10}O_2Br_2$ requires Br = 55·9 per cent.

1 : 5-*Dibromo*-1-*methyl*cyclo*pentane*-2-*carboxylic acid* darkens at about 150°, and decomposes vigorously and becomes black at about 164°.

It is readily soluble in ether, chloroform, or benzene, but sparingly so in light petroleum or formic acid in the cold. When boiled with formic acid, it decomposes vigorously, and the solution becomes violet-black and deposits black flocks on the addition of water.

The dibromo-acid is readily decomposed by boiling with methyl-alcoholic potash, and the solution has an odour of bromoform; it is also decomposed by silver nitrate and nitric acid in the cold with abundant separation of silver bromide.

Oxidation of 1-*Methyl*-Δ^5-cyclo*pentene*-2-*carboxylic Acid to* γ-*Acetobutyric Acid*, $CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO_2H$.*

In this experiment, the pure acid (2 grams) was dissolved in a slight excess of dilute sodium carbonate in a test tube, and ozone led through

---

* In order to become acquainted with the mechanism of the oxidation of closed chain unsaturated acids by ozone, we experimented, in the first instance, with *iso*lauronolic acid.

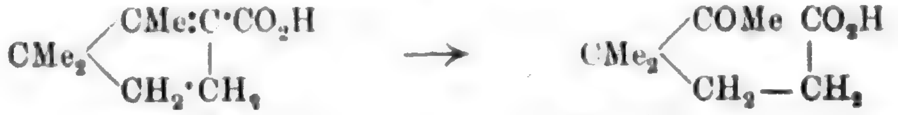
This acid (2 grams) was dissolved in dilute sodium carbonate, and ozone passed for about three hours and until it was no longer absorbed. When the clear solution was acidified, saturated with ammonium sulphate, and extracted with ether in the usual manner, it yielded a syrup which, after remaining in an evacuated desiccator over sulphuric acid for a short time, solidified. After rapidly washing on porous porcelain with light petroleum (b. p. 30—40°), the substance melted at about 47° and proved to be γ-dimethylacetobutyric acid:

0·1297 gave 0·2880 CO_2 and 0·1050 H_2O. C = 60·6; H = 9·0.

$C_8H_{14}O_3$ requires C = 60·8; H = 8·8 per cent.

The acid was dissolved in water, mixed with semicarbazide hydrochloride and sodium acetate, and warmed on the water-bath, when the semicarbazone separated in glistening plates. It crystallised from water as a felted mass of needles, and decomposed vigorously at about 187°. A direct comparison showed that this semicarbazone was identical with that obtained from a specimen of γ-dimethylacetobutyric acid which had been prepared on a previous occasion (Trans., 1898, **73**, 844).

The almost quantitative formation of this keto-acid by the oxidation with ozone is probably the most conclusive evidence of the constitution of *iso*lauronolic acid:



*iso*Lauronolic acid. γ-Dimethylacetobutyric acid.

the solution. When the ozone was no longer absorbed and passed freely, the product was acidified, saturated with ammonium sulphate, and extracted five times with ether. The ethereal solution, after drying over calcium chloride and evaporating, deposited a syrup which yielded bromoform on treatment with bromine and potassium hydroxide, and gave an immediate precipitate with semicarbazide hydrochloride and sodium acetate. The *semicarbazone* was collected and crystallised from water, from which it separated in needles, which softened at 170° and melted at 174—176°. It was found to contain water of crystallisation :[*]

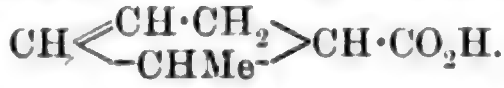
0·1336 gave 0·2010 CO_2 and 0·0900 H_2O. C = 40·7 ; H = 7·4.
0·1153 „ 21·2 c.c. nitrogen at 19·5° and 749 mm. N = 20·7.
$C_7H_{13}O_3N_3,H_2O$ requires C = 41·0 ; H = 7·3 ; N = 20·5 per cent.

These results seemed to point to a ketonic acid, $C_6H_{10}O_3$, probably γ-acetobutyric acid, $CH_3\cdot CO\cdot[CH_2]_3\cdot CO_2H$, and to confirm this the semicarbazone of this acid was prepared from the specimen originally obtained by Bentley and Perkin (Trans., 1896, **69**, 1513). It melted at 176°, and, when mixed with the specimen described above, no alteration in the melting point could be detected. The semicarbazone of the acid from the ozone oxidation was decomposed by warming with dilute hydrochloric acid, the acid extracted with ether, and the ethereal solution evaporated, when a syrup was obtained which, on standing in the air, soon crystallised. The crystals were drained on porous porcelain, and analysed with the following result :

0·1247 gave 0·2256 CO_2 and 0·0922 H_2O. C = 49·3; H = 8·2.
$C_6H_{10}O_3,H_2O$ requires C = 48·7 ; H = 8·1 per cent.

This substance melts at 36° and was proved, by direct comparison, to be the characteristic *hydrate* of *γ-acetobutyric acid*.

1-*Methyl*-Δ^4-cyclo*pentene*-2-*carboxylic Acid*,



$$CH\negthickspace\begin{array}{l}\diagup CH\cdot CH_2 \diagdown\\ \diagdown\!-CHMe-\diagup\end{array}\negthickspace CH\cdot CO_2H.$$

It is explained on p. 585 that this acid esterifies very readily, a property which renders its separation from the Δ^5-acid a comparatively easy matter. The ester obtained as the result of the fifth fractional esterification distilled constantly at 120—122° (100 mm.), and was pure *ethyl* 1-*methyl*-Δ^4-cyclo*pentene*-2-*carboxylate* :

0·1324 gave 0·3220 CO_2 and 0·0958 H_2O. C = 66·4 ; H = 8·0.
$C_7H_{10}O_2$ requires C = 66·7 ; H = 7·9 per cent.

---

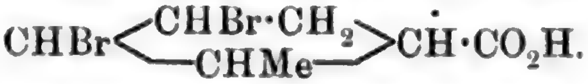
[*] This semicarbazone had been prepared by Bentley and Perkin and dried at 100°, when the specimen gave numbers agreeing with the formula $C_7H_{13}O_3N_3$.

This ester possesses in a marked degree the pungent and most unpleasant odour characteristic of so many of the esters of cyclic unsaturated acids. The pure ester (20 grams) was now mixed with 100 c.c. of 10 per cent. methyl-alcoholic potash, and allowed to remain overnight. Water was then added, the clear solution saturated with carbon dioxide, evaporated until free from alcohol, acidified, the oily acid extracted with ether, and the ethereal solution carefully dried over calcium chloride. The ether was then evaporated, and the acid distilled under reduced pressure, when the whole quantity passed over at 164—165° (100 mm.):

0·1032 gave 0·2634 CO_2 and 0·0870 H_2O. $C = 69·7$; $H = 9·3$.
$C_9H_{14}O_2$ requires $C = 70·1$; $H = 9·1$ per cent.

1-*Methyl*-Δ^4-cyclo*pentene*-2-*carboxylic acid* is a viscid oil, and possesses a pungent odour similar to that of the higher fatty acids. It behaves as an unsaturated acid, since its solution in chloroform rapidly decolorises bromine, and the sodium salt instantly decolorises permanganate. When it was boiled with concentrated aqueous potassium hydroxide for five minutes, it became dark brown, and, on acidifying, yielded a liquid acid, so that conversion into the Δ^5-acid does not appear to take place under these conditions.

4 : 5-*Dibromo*-1-*methyl*cyclo*pentane*-2-*carboxylic Acid*,



$$\mathrm{CHBr}<\begin{matrix}\mathrm{CHBr\cdot CH_2}\\ \mathrm{CHMe}\end{matrix}>\mathrm{CH\cdot CO_2H}.$$

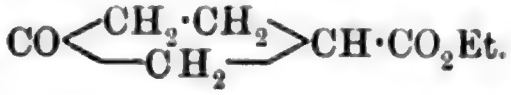
In preparing this acid, pure 1-*methyl*-Δ^4-cyclo*pentene*-2-*carboxylic acid* (1·35 grams) was dissolved in three volumes of chloroform, cooled to $-10°$, and then titrated with a solution of bromine in chloroform. The colour disappeared instantly at first and rather slowly at the close of the reaction, and remained when 1·65 grams had been added, the end point being fairly sharp. Theoretically, 1·7 grams of bromine should be absorbed by 1·35 grams of the unsaturated acid. The product was allowed to evaporate on a clock glass, when a syrup remained which gradually crystallised and became semi-solid. In contact with porous porcelain, the oil was slowly absorbed, and the colourless residue separated from light petroleum (b. p. 50—60°) in crusts which melted, not very sharply, at 106—108°:

0·2850 gave 0·3740 AgBr. $Br = 55·8$.
$C_7H_{10}O_2Br_2$ requires $Br = 55·9$ per cent.

Oxidation of 1-*Methyl*-Δ^4-cyclo*pentene*-2-*carboxylic Acid to* α-*Methyltricarballylic Acid*, $CO_2H\cdot CHMe\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$.

This oxidation was carried out by passing ozone into the solution of the sodium salt of the acid, the conditions of experiment being the same as those already described in the case of the oxidation of the Δ^5-acid. The product was warmed on the water-bath to decompose any unchanged ozonide, acidified, saturated with ammonium sulphate, and repeatedly extracted with ether. When the ether was removed by evaporation, a dark brown oil was obtained, which showed no signs of crystallisation after remaining for several days over sulphuric acid in an evacuated desiccator. It was dissolved in hot water, the solution filtered, and heated on the water-bath with an excess of potassium dichromate and sulphuric acid. After saturating with ammonium sulphate, the green solution was extracted several times with ether on the machine, and the ethereal solution evaporated, when a nearly colourless syrup was obtained which soon became semi-solid. In contact with a little concentrated hydrochloric acid, the oily impurity was soon dissolved, leaving a colourless, crystalline acid, which was drained on porous porcelain and twice recrystallised from hydrochloric acid, from which it separated in small, glistening prisms melting at 177°. That this acid was α-methyltricarballylic acid (m. p. 180°) was proved by mixing it with a specimen which had been prepared from the sodium derivative of methylmalonic ester by condensation with fumaric ester (Auwers, Köbner, and Meyenburg, *Ber.*, 1891, **24**, 2891), when the mixture melted at 178—180°.

The Action of Magnesium Methyl Iodide on Ethyl cyclo*Pentanone*-3-*carboxylate*,



$$\mathrm{CO}\left<\begin{array}{c}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2}\end{array}\right>\mathrm{CH\cdot CO_2Et}.$$

The *ethyl* cyclo*pentanonecarboxylate* required for these experiments was prepared by digesting the free acid (Kay and Perkin, Trans., 1906, **89**, 1646), in quantities of 50 grams, with a 3 per cent. solution of hydrogen chloride in alcohol (180 grams) for six hours on the water-bath. The product was mixed with three volumes of ether, the ethereal solution repeatedly washed with dilute sodium carbonate, dried over calcium chloride, and evaporated. On fractionation under reduced pressure, the ester distilled constantly at 142—143° (40 mm.) as a colourless oil possessing an odour somewhat resembling that of apples:

0·1873 gave 0·4186 CO_2 and 0·1337 H_2O. C = 61·0; H = 7·9.

$C_8H_{12}O_3$ requires C = 61·5; H = 7·7 per cent.

This ester, in quantities of 30 grams, was slowly added from a dropping funnel to an ethereal solution of magnesium methyl iodide (containing 20 grams of magnesium), the contents of the containing vessel being rapidly stirred by a turbine and the whole carefully cooled with ice and salt. After remaining for four days, the product was cautiously decomposed by ice and very dilute hydrochloric acid, the ethereal layer separated, and the aqueous solution repeatedly extracted with ether. The combined ethereal extracts were dried over calcium chloride and, in order to avoid loss of any volatile hydrocarbon, the ether was slowly distilled off with the aid of a column. The residue was distilled in steam and the distillate,* which contained a considerable quantity of an oil with an odour of peppermint, was extracted with ether, the ethereal solution dried and evaporated as before, and the oil fractionated under reduced pressure.

A good deal of oil passed over below 100° (200 mm.), and there was a large fraction at 100—125° (50 mm.) and a further considerable fraction at 115—125° (15 mm.). After repeated distillation, these fractions yielded a mobile oil, boiling at 150—155° under the ordinary pressure, and a more viscid oil, distilling at 100—105° (30 mm.).

The oil distilling at 150—155° was twice distilled over sodium, when almost the whole quantity passed over at about 150°:

0·1836 gave 0·5990 CO_2 and 0·1955 H_2O. $C=88·9$; $H=11·8$.

C_9H_{14} requires $C=88·5$; $H=11·5$ per cent.

1-*Methyl*-3-iso*propenyl*cyclo*pentene* (compare p. 575) is a colourless oil with a pronounced odour of lemons and peppermint.

It combines with hydrogen bromide and with bromine, but the amount of material available was too small to allow of these additive products being investigated.

The fraction boiling at 100—105° (30 mm.) gave the following results on analysis:

0·1912 gave 0·5374 CO_2 and 0·1930 H_2O. $C=76·7$; $H=11·2$.

$C_9H_{16}O$ requires $C=77·1$; $H=11·3$ per cent.

1-*Methyl*-3-iso*propenol*cyclo*pentene* (compare p. 575) is a rather viscid oil with a strong odour of terpineol and peppermint, it is sparingly soluble in water, and its solution in acetic anhydride gives a deep crimson, nearly as intense as solution of permanganate, on the addition of a drop of sulphuric acid. In order to obtain the corresponding terpin, this oil (5 grams) was shaken with 300 c.c. of 5 per cent. sulphuric acid during several days, and until it had completely dissolved. The clear solution was extracted once with ether to remove any unchanged carbinol, it was then saturated with ammonium sulphate, and extracted ten times, on the machine, with large quantities of ether. The extracts were dried over calcium chloride and evaporated, when a viscid, almost colourless oil was obtained, which on analysis gave numbers closely approximating to those required by the formula $C_9H_{18}O_2$. This syrup, which is probably a mixture of *cis*- and *trans*-modifications, gradually became semi-solid, and, in contact with porous porcelain, the oil was rapidly absorbed, leaving a colourless mass which, after crystallisation from a very small quantity of water, yielded the following results on analysis:

---

* A large quantity of dark-coloured resinous matter remained in the distilling flask.

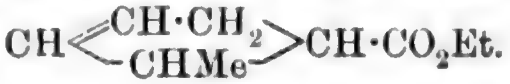
0·1135 gave 0·2813 H_2O and 0·1146 H_2O. $C = 67·6$; $H = 11·2$.

$C_9H_{18}O_2$ requires $C = 68·3$; $H = 11·4$ per cent.

1-*Hydroxy*-1-*methyl*-3-iso*propenol*cyclo*pentane* (compare p. 575) softens at 70° and melts at 75°, and is excessively soluble in water, but rather sparingly so in cold ether. It dissolves readily in warm ether, and crystallises slowly from the concentrated solution in feathery groups. Its solution in acetic anhydride gives, with a trace of sulphuric acid, a pink solution which soon fades.

The terpin dissolves in fuming aqueous hydrobromic acid, but the solution soon clouds, and an oil separates which has a penetrating and highly characteristic odour resembling that of sage and carraway seeds.

The Action of Magnesium Methyl Iodide on Ethyl 1-*Methyl*-Δ^4-cyclo*pentene*-2-*carboxylate*,



$$CH\begin{matrix}\diagup CH\cdot CH_2 \diagdown \\ \diagdown CHMe \diagup\end{matrix}CH\cdot CO_2Et.$$

The conversion of this ester into 1-*methyl*-2-iso*propenol*-Δ^4-cyclo*pentene* takes place almost quantitatively under the following conditions. Magnesium (12 grams) is converted into magnesium methyl iodide in the usual manner, and, after cooling well, ethyl methyl*cyclo*pentenecarboxylate (26 grams) is gradually added. There is little action on mixing, but afterwards the liquid gradually comes to the boil. After four hours, the product is cautiously decomposed by water and dilute hydrochloric acid, the ethereal solution washed well, evaporated, and the residue left in contact with methyl-alcoholic potash (10 grams KOH) overnight. Water and ether are then added, and the ethereal solution washed well,* dried over calcium chloride, evaporated, and the residue fractionated under reduced pressure, when almost the whole quantity passes over at 95° (30 mm.):

0·1212 gave 0·3420 CO_2 and 0·1264 H_2O. $C = 76·9$; $H = 11·6$.

$C_9H_{16}O$ requires $C = 77·0$; $H = 11·4$ per cent.

---

* The aqueous layer yields, on acidification and extraction with ether, a mere trace of unchanged acid, showing that the conversion into the carbinol was practically complete.

1-*Methyl*-2-iso*propenol*-Δ^4-cyclo*pentene* is a colourless, viscid liquid, which possesses a very pungent odour of terpineol and peppermint. It yields an intense reddish-brown coloration when a drop of sulphuric acid is added to its solution in acetic anhydride. When the pure substance is quickly added to an acetic acid solution of hydrogen bromide (saturated at 0°), it dissolves with considerable evolution of heat, and the solution becomes purple, then brown, and, finally, dark green.

If, however, the oil is gradually added to the hydrobromic acid solution, cooled in ice, a clear solution is produced, which rapidly clouds and from which an oily layer soon separates. When this mixture is allowed to stand, the lower layer becomes dark brown and the oil a chartreuse-green, and, after twelve hours, the liquid becomes an intense sage-green and the oil red. It is unfortunate that it was not found possible to convert this carbinol into a crystalline urethane or nitroso-chloride, and the only crystalline derivative of any value for its identification is the terpin described below. When the carbinol is mixed with phenylcarbimide and allowed to remain at the ordinary temperature for several days, crystals of diphenylcarbamide slowly separate.

An attempt was made to prepare a crystalline nitroso-chloride by leaving the pure carbinol (1·5 c.c.) in contact with ethyl nitrite (6 c.c. of a 15 per cent. alcoholic solution) and concentrated hydrochloric acid (1·5 c.c.), but the nitroso-chloride produced was a thick syrup. A comparative experiment showed that, under exactly the same conditions, ordinary terpineol is rapidly converted into its crystalline nitroso-chloride.

5-*Hydroxy*-1-*methyl*-2-iso*propenol*cyclo*pentane* (see p. 578).—This crystalline terpin is produced in a fairly good yield under the following conditions. The carbinol (10 grams) is shaken on the machine with water (600 c.c.) and sulphuric acid (3 grams), when, even after several days, a considerable brown, oily layer separates on standing.

The product was filtered and extracted once with a little ether,* the aqueous solution was then saturated with ammonium sulphate, and extracted five times on the machine with the same solvent. After drying over calcium chloride and evaporating, the ethereal solution deposited a viscous syrup which gradually crystallised, and, in contact with porous porcelain, a good deal of oily impurity was readily absorbed, leaving a colourless, crystalline mass. The substance was dissolved in much pure ether, filtered, and the filtrate concentrated considerably, when, on standing, groups of colourless needles separated, which were collected, washed with ether, and dried over sulphuric acid in an evacuated desiccator. The mother liquors of these crystals deposited, on concentration, a further crop of the same substance, and there was no evidence of the presence of an isomeride:

---

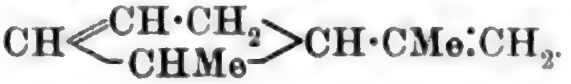
* This ethereal extract yielded, on evaporation, a brown oil which contained, besides unchanged carbinol, a considerable quantity of very high boiling resinous matter.

0·1184 gave 0·2964 CO_2 and 0·1250 H_2O. C = 68·3; H = 11·7.

$C_9H_{18}O_2$ requires C = 68·3; H = 11·4 per cent.

5-*Hydroxy*-1-*methyl*-2-iso*propenol*cyclo*pentane* melts at 70—72°, and is very similar to terpin in appearance. It is excessively soluble in water or alcohol, sparingly so in cold benzene or light petroleum in the cold. It dissolves readily in warm benzene, and separates, on cooling, as an oil which gradually crystallises. When it is warmed with an acetic acid solution of hydrogen bromide (saturated at 0°), it dissolves with slight evolution of heat, and the solution soon clouds and an oil separates. On standing for several days, the oil remains almost colourless, but the solvent becomes an intense brownish-red.

1-*Methyl*-2-iso*propenyl*-Δ^4-cyclo*pentene*,



$$\mathrm{CH}<\begin{matrix}\mathrm{CH\cdot CH_2}\\ \mathrm{CHMe}\end{matrix}>\mathrm{CH\cdot CMe{:}CH_2}.$$

It has been mentioned in the introduction (p. 578) that the elimination of water from 1-methyl-2-*iso*propenol-Δ^4-*cyclo*pentene results in the formation, under the most favourable conditions, of only very small quantities of the above terpene, the principal substances always obtained being condensation products of higher molecular weight. When the carbinol is heated with potassium hydrogen sulphate under the usual conditions, it yields principally a high boiling brown oil, and, if anhydrous oxalic acid is employed, the result is a viscid, almost black, product. The carbinol dissolves in anhydrous formic acid with a pink colour, and, when heated on the water-bath, the solution separates into two layers, the lower acid layer is dark brown, whereas the upper oily layer is nearly colourless. If the product is distilled, some methyl*iso*propenyl*cyclo*pentene is obtained, but the yield is most unsatisfactory, owing to the formation of large quantities of polymerised hydrocarbons.

Attempts were then made to bring about the elimination of water at the ordinary temperature by leaving the carbinol in contact with a large excess of magnesium methyl iodide for a week, but little action took place and almost the whole of the carbinol was recovered unchanged. The best results were ultimately obtained by heating the carbinol with twice its weight of succinic anhydride* for fifteen minutes and then distilling in steam, when a colourless oil passed over, leaving a dark brown condensation product in the distillation flask.

---

* Phthalic anhydride may also be used, but with less satisfactory results.

The distillate was extracted with ether, the ethereal solution dried over calcium chloride, evaporated, and the residue fractionated, first alone and then three times over sodium, when a colourless oil was obtained which distilled at 143—145° (770 mm.):

0·2120 gave 0·6785 CO_2 and 0·2230 H_2O. C = 87·3; H = 11·6.

C_9H_{14} requires C = 88·5; H = 11·5 per cent.

1-*Methyl*-2-iso*propenyl*-Δ^4-cyclo*pentene* has a distinct odour of lemons, and oxidises very readily in the air, a fact which accounts for the somewhat low numbers obtained in the above analysis. When a small quantity of the terpene was placed over water in a tube sealed at one end, the absorption of oxygen took place very rapidly, and overnight the level of the water had risen to almost exactly one-fifth of the volume of the air taken. The solution of the terpene in acetic anhydride gives an intense blood-red coloration when a trace of sulphuric acid is added, and, on warming, the colour changes to violet-black. The terpene does not dissolve in an acetic acid solution of hydrogen bromide (saturated at 0°), but a good deal of heat is liberated, and the oil becomes brown, then blood-red, and, after several hours, a deep sage-green. The dark brown condensation products, obtained in such quantities during the preparation of the terpene, have properties closely resembling those described in more detail in the case of the corresponding experiments in the Δ^5-series (p. 597). When fractionated, a good deal of a yellowish-brown oil distilled at 170—175° (20 mm.), and evidently consisted of the polymeride, $(C_9H_{14})_2$; it oxidised very rapidly in the air, and gave only approximate results on analysis.

The Action of Magnesium Methyl Iodide on Ethyl 1-*Methyl*-Δ^5-cyclo*pentene*-2-*carboxylate*,

$$CH{<}\begin{matrix}CH_2\cdot CH_2\\ CMe\text{——}\end{matrix}{>}CH\cdot CO_2Et.$$

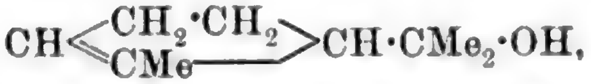
It has been pointed out in the introduction (p. 579) that this decomposition proceeds abnormally, and gives only a very small yield of the corresponding tertiary alcohol. In several experiments, the pure ester (37 grams) was treated with magnesium methyl iodide (containing 17 grams of magnesium), and the product was left overnight and decomposed by dilute hydrochloric acid in the usual manner.

The ethereal solution was washed with dilute sulphurous acid to remove iodine, dried over calcium chloride, and evaporated, when a brown oil was obtained, which, by distillation under reduced pressure, was separated into three fractions: 80—120° (40 mm.), 170—172° (18 mm.), and 225—230° (15 mm.). The lowest fraction yielded, on careful fractionation, a small quantity of a hydrocarbon, distilling at about 147° under the ordinary pressure, and about three grams of an oil boiling at 97—100° (30 mm.). The oil of boiling point 147° is doubtless the terpene, but the quantity was so small and the substance oxidised so rapidly in the air that no analysis was attempted. The oil of boiling point 97—100° (30 mm.) had a strong odour of peppermint, and when dissolved in acetic anhydride gave, on the addition of a trace of sulphuric acid, a red coloration, which was distinctly bluer than that yielded by the corresponding Δ^4-carbinol (p. 594) under these conditions. The following results were obtained on analysis:

0·1965 gave 0·5450 CO_2 and 0·1940 H_2O. $C = 75{\cdot}7$; $H = 11{\cdot}0$.

$C_9H_{16}O$ requires $C = 77{\cdot}0$; $H = 11{\cdot}4$ per cent.

There can be no doubt that this substance is 1-*methyl*-2-iso*propenol*-Δ^5-cyclo*pentene*,


$$CH\Big\langle\begin{matrix}CH_2\cdot CH_2\\ CMe\text{——}\end{matrix}\Big\rangle CH\cdot CMe_2\cdot OH,$$

but the amount of material at our disposal was so small that it was impossible to investigate its properties.

The fraction 170—172° (18 mm.) was distilled over sodium without altering its boiling point and then analysed:

0·1146 gave 0·3613 CO_2 and 0·1200 H_2O. $C = 86{\cdot}0$; $H = 11{\cdot}6$.

$(C_9H_{14})_2$ requires $C = 88{\cdot}5$; $H = 11{\cdot}5$ per cent.

Subsequently, it was discovered that this very viscid hydrocarbon is very rapidly oxidised in the air, and this fact accounts for the low numbers obtained in the above analysis. After remaining in a loosely-corked test-tube for a week a second analysis was made, and the substance found to contain only $C = 80{\cdot}1$, and $H = 10{\cdot}3$.

A small quantity of the hydrocarbon, left in contact with air in a tube over water, absorbed the whole of the oxygen in a few hours. No further experiments were made either with this hydrocarbon or with the higher fraction, 225—230° (15 mm.), mentioned above.

The authors are greatly indebted to the Research Fund Committees, both of the Royal Society and of the Chemical Society, for grants, which have largely defrayed the heavy cost of this investigation.

THE UNIVERSITY,
MANCHESTER.

LIV.—*A β-Lactonic Acid from Acetone and Malonic Acid.*

By ANDREW NORMAN MELDRUM (Carnegie Research Fellow).

THE condensation between acetone and malonic acid might well be expected to yield *iso*propylenemalonic acid, $\mathrm{Me_2C{:}C(CO_2H)_2}$, and from this, by the loss of carbon dioxide, dimethylacrylic acid,

$$\mathrm{Me_2C{:}CH{\cdot}CO_2H},$$

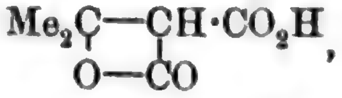
might result. Actually the condensation, as it proceeds in presence of acetic anhydride* (Massot, *Ber.*, 1894, **27**, 1225) or ammonium malonate (Knoevenagel, D.R.-P. 162281) does result in dimethylacrylic acid.

Ethyl *iso*propylenemalonate, $\mathrm{Me_2C{:}C(CO_2Et)_2}$, is produced by heating together ethyl malonate, acetone, acetic anhydride, and zinc chloride. On hydrolysis of the ester, *iso*propylenemalonic acid is obtained (Meyenberg, *Ber.*, 1895, **28**, 785).

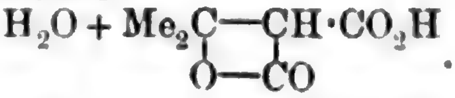
Wishing to study the reaction between acetone and malonic acid, the author, on Professor Japp's suggestion, employed as condensing agent acetic anhydride with the addition of a little sulphuric acid. Under these conditions, the reaction, which proceeds smoothly and without the application of heat, yields in the course of twenty-four hours a crystalline acid melting at 97°, which is a new condensation product of acetone and malonic acid, since it is neither dimethylacrylic acid (m. p. 70°) nor *iso*propylenemalonic acid (m. p. 170—171°).

Analysis and molecular weight determination lead to the formula $C_6H_8O_4$ for the substance, which is evidently formed according to the equation:

$$C_3H_6O + C_3H_4O_4 = H_2O + C_6H_8O_4.$$

Titration with alkali showed that the acid is monobasic, so that it is probably a lactonic acid. Treatment with excess of alkali, with the object of obtaining direct evidence of the presence of the lactonic group, was found to cause disruption into acetone and malonic acid. Nevertheless, there can hardly be a doubt that the substance, considering the method of its formation, has the constitution  $\begin{array}{l}\mathrm{Me_2C{-}CH{\cdot}CO_2H}\\ \quad\mathrm{O{-}CO}\end{array}$, that is, it is the β-lactone of *β-hydroxyisopropylmalonic* acid. The formation of the lactone may therefore be represented as follows:

$$\mathrm{Me_2CO + CH_2(CO_2H)_2 = Me_2C(OH){\cdot}CH(CO_2H)_2 =}$$



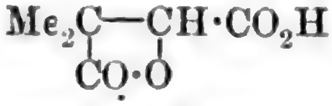
$$\mathrm{H_2O +} \begin{array}{l}\mathrm{Me_2C{-}CH{\cdot}CO_2H}\\ \quad\quad\mathrm{O{-}CO}\end{array}.$$

---

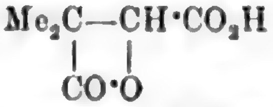
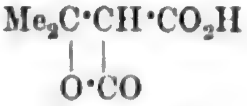
* Komnenos (*Annalen*, 1883, **218**, 147, 168), using acetic acid as condensing agent, obtained crotonic acid, $\mathrm{MeCH{:}CH{\cdot}CO_2H}$, from malonic acid and paraldehyde, but found that there was no reaction between malonic acid and acetone.

Google

Closely related to this β-lactone is one which has been described by Baeyer and Villiger (*Ber.*, 1897, **30**, 1954, see also Fichter and Hirsch, *Ber.*, 1900, **33**, 3270). The parent substance of Baeyer and Villiger's lactone is *as*-dimethylmalic acid, $Me_2C(CO_2H)\cdot CH(OH)\cdot CO_2H$ (in which the relative positions of the $\cdot OH$ and $\cdot CO_2H$ groups are precisely the reverse of what they are in the isomeric β-hydroxy*iso*propylmalonic acid), and the lactone itself is

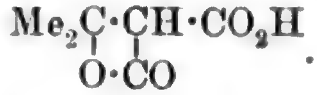

$\begin{array}{l} Me_2C - CH\cdot CO_2H \\ \quad\ \ | \qquad | \\ \quad\ CO\cdot O \end{array}$.

It is remarkable that the only two β-lactones known in the fatty series should be isomerides, and should both contain the grouping $Me_2\cdot \dot{C}\cdot \dot{C}H\cdot CO_2H$. It would appear that the grouping, $Me_2\dot{C}\cdot \dot{C}H_2$ is specially adapted to the formation of β-lactones, although it is difficult to find an explanation of this interesting point. The following comparison shows that the two lactones, closely related as they are, differ considerably in properties:

	 $\begin{array}{l} Me_2C - CH\cdot CO_2H \\ \quad\ \ | \quad\ | \\ \quad\ CO\cdot O \end{array}$ (Baeyer and Villiger).	 $\begin{array}{l} Me_2C\cdot CH\cdot CO_2H \\ \quad\ \ | \quad | \\ \quad\ O\cdot CO \end{array}$ (Meldrum).
Melting point	45—47°.	97°.
With water	Gives $C_6H_8O_4, H_2O$.	Gives no compound.
Hydrolysis by dilute acid.	Gives *as*-dimethylmalic acid.	Gives malonic acid and acetone.
Action of heat	Gives the anhydride of *as*-dimethylmalic acid, without elimination of carbon dioxide.	Gives carbon dioxide and resinous products.

EXPERIMENTAL.

*β-Lactone of β-Hydroxy*iso*propylmalonic Acid,*


$\begin{array}{l} Me_2C\cdot CH\cdot CO_2H \\ \quad\ \ | \quad\ | \\ \quad\ O\cdot CO \end{array}$.

When malonic acid (104 grams), acetone (116 grams), and acetic anhydride (204 grams) are mixed there is little change, but on addition of sulphuric acid (5 c.c.) a rise in temperature occurs and the malonic acid soon dissolves. After twenty-four hours the liquid gives a crystalline deposit, which can be increased by leaving in a freezing mixture for a short time. The yield of the crude substance is 65—70 grams, and is apparently not increased by varying the proportions of material or the other conditions of the experiment. The mother liquor, on evaporation at the ordinary temperature, yields only impure malonic acid (30 grams). The solid is collected, washed with cold water, and crystallised from acetone, from which it separates in colourless, transparent four-sided plates or prisms obliquely terminated, and melting at 97°.

When the temperature is raised above 97° the liquid turns yellow and finally brown, while carbon dioxide is evolved, the decomposition from 130° upwards being rapid. In hot water, ether, alcohol, or chloroform, the substance is much more soluble than in the cold solvent:

0·2934 gave 0·5378 CO_2 and 0·1465 H_2O. C = 49·98; H = 5·55.
$C_6H_8O_4$ requires C = 50·00; H = 5·55 per cent.

The lactone is decomposed by hydrobromic acid in the cold, with separation of malonic acid; when digested with baryta water, a precipitate of barium malonate is produced. Heated with aniline, it yields acetone, carbon dioxide, and acetanilide.

A determination of the molecular weight in acetone solution by the boiling-point method (in the Lumsden-Walker apparatus), which Mr. W. E. S. Turner, M.Sc., kindly undertook, gave the following numbers:

Weight of substance, in grams.	Elevation.	Volume, in c.c.	Mol. wt.
1·51	1·03°	27·1	123
	0·93	29.4	125
	0·84	32·4	126
	0·74	36·3	127·5

(The boiling point elevations have been corrected for the change in boiling point due to the increase of liquid and therefore of pressure in the boiling tube.) As the solution becomes more dilute, the molecular weight seems to increase, a phenomenon often observed in acetone solution. On plotting the molecular weight against the elevation, the molecular weight at zero elevation, that is, at infinite dilution, is found to be 139. $C_6H_8O_4$ requires mol. wt. = 144.

The equivalent of the acid was determined by titration with standard alkali (of which 4293 c.c. neutralise the equivalent in grams of any acid):

$$0{\cdot}4405 \text{ required } 13{\cdot}3 \text{ c.c. Equivalent} = \frac{0{\cdot}4405 \times 4293}{13{\cdot}3} = 142{\cdot}2.$$

The potassium and sodium salts, which are very soluble in water, are obtained by evaporating the respective solutions in a vacuum desiccator. The *potassium* salt consists of prisms or striated plates. Two different specimens were analysed:

0·3722 gave 0·1576 K_2SO_4. K = 19·03.
0·3211 „ 0·1396 „ K = 19·54.
$C_6H_7O_4K,H_2O$ requires 19·56 per cent.

The *sodium* salt consists of six-sided plates :

0·4747 gave 0·2003 Na_2SO_4. Na = 13·67.
$C_6H_7O_4Na$ requires 13·85 per cent.

The sodium and potassium salts are white, but they turn yellow in the course of two or three months.

The *silver* salt is obtained as a white, microcrystalline precipitate on adding silver nitrate to a solution of the sodium salt. It darkens when kept for some time :

0·1948 gave 0·0838 Ag. Ag = 43·01.
$C_6H_7O_4Ag$ requires 43·02 per cent.

The *barium* salt is very soluble in water and was not analysed. On boiling its solution, a white substance separated which was found to consist of barium malonate :

0·293 gave 0·2708 $BaSO_4$. Ba = 54·41.
$C_3H_2O_4Ba,H_2O$ requires Ba = 53·4 per cent.

The readiness with which the β-lactone of β-hydroxy*iso*propylmalonic acid decomposes, either into malonic acid and acetone, or in other directions, has proved a great hindrance to its investigation The author has commenced the study of its behaviour with various reagents, in particular with phosphorus pentachloride and with ammonia.

The author, who first prepared this substance nearly four years ago in the Chemical Department of Aberdeen University, but had to discontinue the investigation for some time, feels grateful to Professor Japp and to Professor Perkin for the interest they have shown in it. The expenses of the investigation have been defrayed by the Executive Committee of the Carnegie Trust for the Universities of Scotland.

CHEMICAL DEPARTMENT,
THE UNIVERSITY,
MANCHESTER.

LV.—*Derivatives of para-Diazoiminobenzene.*

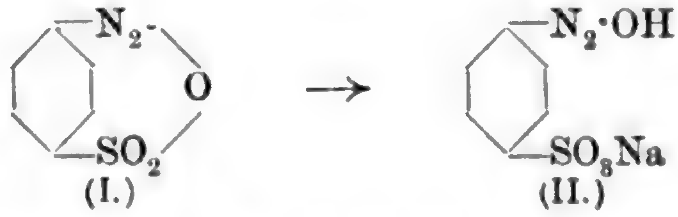
By Gilbert T. Morgan and Frances M. G. Micklethwait.

A group of aromatic diazo-derivatives exists in which the original diazonium complex may be considered to have undergone condensation with another reactive substituent of the aromatic nucleus. In general, this condensation may be regarded as being due to the operation of one or both of two factors, namely, internal salt formation and the tendency for ring formation. Accordingly the diazo-compounds produced by internal condensation may be classified under the three following headings:

1.—*Internal Diazonium Salts.*

The best known substances of this class are the so-called diazosulphonic acids, of which "diazobenzenesulphonic acid," derived from sulphanilic acid, is the simplest example. This compound and its homologues are produced even in the presence of strong mineral acids, and they are undoubtedly internal salts,* arising from the interaction of the powerfully basic diazonium complex and the strongly acid sulphonic group.

That the tendency for ring formation plays little or no part in the production of these internal diazonium salts, is evident from the fact that they are obtained from all aromatic aminosulphonic acids, whatever be the orientation of their aminic and sulphonic groups. Metanilic and the heteronuclear aminonaphthalenesulphonic acids, for example, furnish these diazonium salts with the same readiness as sulphanilic and naphthionic acids. These condensation products have the properties of sulphonates of moderately strong bases, and when treated with a stronger base, such as an alkali hydroxide, they are decomposed, the heterocyclic ring undergoing fission in the following manner:



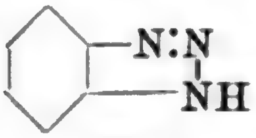
---

* It is somewhat unfortunate that the true nature of these substances is not indicated by their usual designation. Armstrong and Robertson (Trans., 1905, **87**, 1282) have referred to the above compound as benzenediazonium parasulphonate, but this suggestion has not been generally adopted.

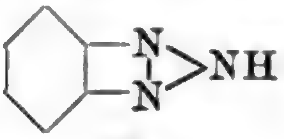
It is on account of this property that these internal diazonium salts have been so extensively employed in the colour industry. Similar internal diazonium salts have also been obtained from the aromatic amino-carboxylic acids.

2.—*Cyclic Diazo-compounds due to Ring Formation.*

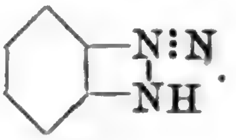
The diazo-derivatives obtained from the ortho-diamines come under this heading. As in these compounds the two contiguous groups are both basic, there can be no question of salt formation. The tendency to ring formation is, however, so strong, and the condensation occurs so readily even in the presence of excess of strong acid, that the intermediate diazonium salts have never been isolated. *o*-Diazoiminobenzene, the simplest example of this class of diazo-compounds, is generally represented by formula III, although two other configurations (IV and V) have been suggested (Trans., 1905, **87**, 75):



(III.)



(IV.)



(V.)

These ortho-diazoimines are distinguished from other cyclic diazo-compounds by their great stability, and no satisfactory method has yet been devised for opening the nitrogen ring present in these substances. Strong hydrolysing agents, whether acid or alkaline, effect no change short of destroying the whole structure of the molecule. It is noteworthy that 1:8-naphthylenediamine yields a peri-diazoimine of this stable type.

Meta- and para-diamines and also the heteronuclear naphthylenediamines (other than the peri-derivative) do not yield diazoimines, and it may therefore be concluded that a close proximity of the amino-groups is required for this condensation. The colourless, stable *o*-diazosulphides obtained by Jacobson and others (*Annalen*, 1893, **277**, 210) from the *o*-aminothiophenols probably belong to this class of diazo-compounds.

3.—*Diazo-compounds due both to Salt and Ring Formation.*

The first diazo-compound discovered by Griess (*Annalen*, 1858, **113**, 201), namely, 4:6-dinitrophenylene-2-diazo-1-oxide, derived from picramic acid, is a typical example of this class. In this instance, the salt-forming tendency existing between the diazonium complex and the phenolic hydroxyl group is reinforced by the ring-forming tendency due to the proximity of the two reacting groups. A similar condensation occurs with the ortho- and para-diazophenols, and also with their nitrated and halogenated derivatives (Hantzsch and Davidson, *Ber.*, 1896, **29**, 1522). 8-Amino-α-naphthol and its derivatives similarly yield peri-diazo-oxides.

That these diazo-oxides result from the combined operation of both salt-forming and ring-forming tendencies is evident from the fact that such condensation products are not obtained from the meta-diazophenols. The ortho-, para-, and peri-diazo-oxides, unlike the ortho- and peri-diazoimines, react with strong acids or alkalis, regenerating respectively either diazonium salts or alkali diazo-oxides, and are accordingly capable of being employed, like the diazonium sulphonates, in the production of azo-colouring matters.

Hitherto no mention has been made of para-diazoimines, the reason being that *p*-phenylenediamine and its homologues have not been found to undergo this condensation on diazotisation. Nevertheless, several condensation products have been obtained, which can be regarded as aryl and acyl derivatives of the hypothetical para-diazoiminobenzene.

Until quite recently, the only compound of this series known was the unstable substance produced by treating a solution of phenyl-*p*-aminobenzenediazonium chloride with caustic potash or ammonia; its existence was first observed by Ikuta (*Annalen*, 1888, **243**, 282) and the compound (X) was afterwards isolated in a state of purity by Hantzsch (*Ber.*, 1902, **35**, 895). In 1905, the authors of the present communication discovered that a very stable series of para-diazoimides could be prepared by treating the diazonium salts of the arylsulphonyl-para-diamines with aqueous sodium acetate. These para-diazoimides were characterised by their yellow colour, sparing solubility, and the facility with which they could be either reconverted quantitatively into the original diazonium salts, or combined with a phenol or naphthol to furnish an azo-compound.

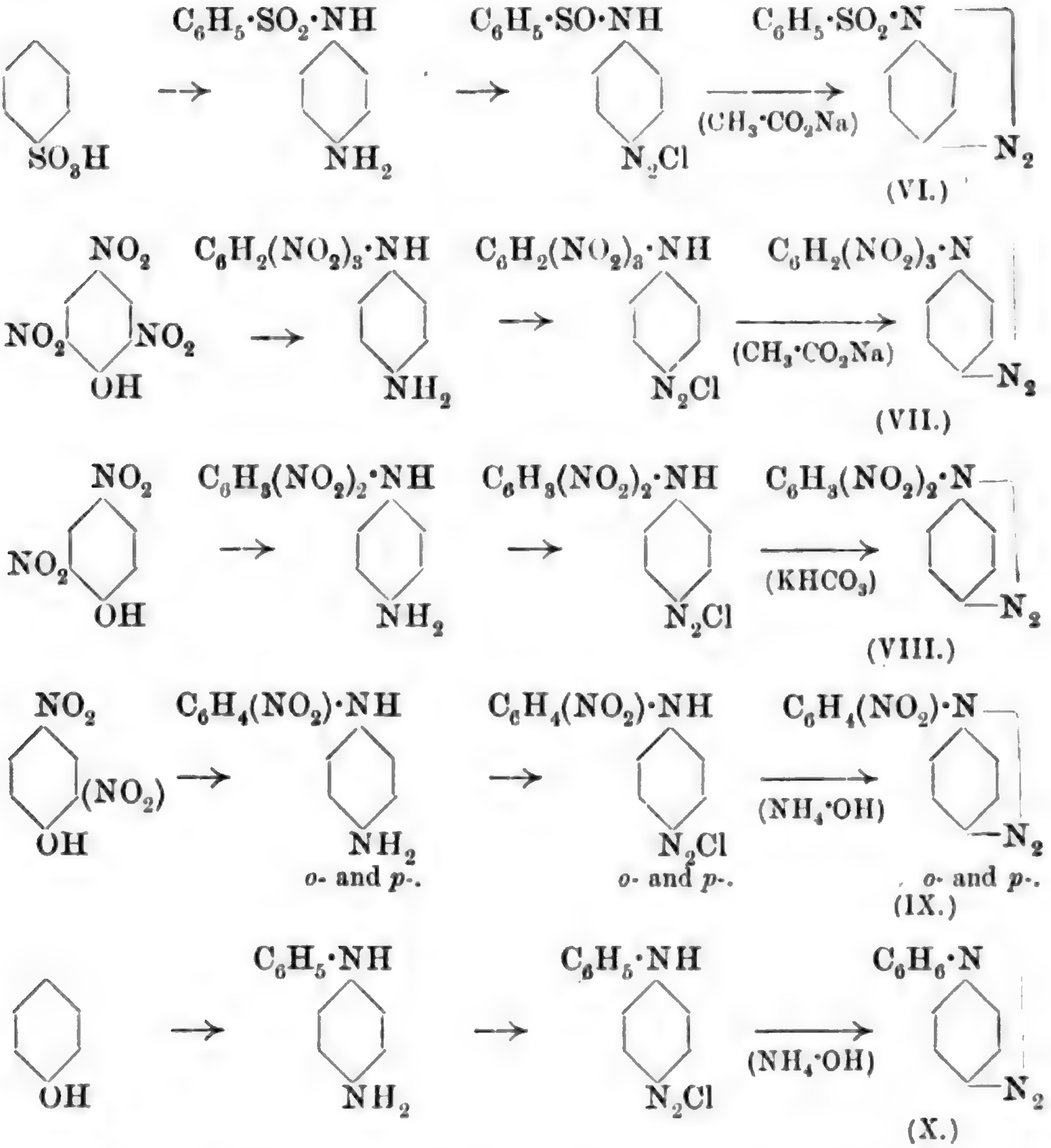
As para-diazoimides were not obtained when the arylsulphonyl groups were replaced by other acyl groups, further experiments were made in order to ascertain whether this condensation was due to some specific property of the arylsulphonyl group, apart from its acidic nature. The results recorded in the present communication show that a similar result can be obtained when the sulphonyl group is replaced by a picryl radicle which, although comparable with the former group in acidic character, is, nevertheless, quite different in chemical structure. The observations described in the experimental section also demonstrate that the stability of the diazoimine is determined by the acidic character of the substituent attached to one of the aminic nitrogen atoms, for as the nitro-groups are successively eliminated from the picryl substituent, the resulting diazoimines become increasingly unstable until from 2-nitrophenyl-*p*-phenylenediamine a diazoimine is obtained which is as readily decomposable as Hantzsch's explosive phenyl-*p*-phenylenediazoimine (*loc. cit.*).

The following series of diamines was examined: 2 : 4 : 6-trinitrophenyl-*p*-phenylenediamine, 2 : 4-dinitrophenyl-*p*-phenylenediamine, 4-nitrophenyl-*p*-phenylenediamine, and 2-nitrophenyl-*p*-phenylenediamine, and the experiments showed that as the acidic character of the substituent diminished the readiness with which condensation occurred also decreased. The diazoimine (VII) from 2 : 4 : 6-trinitrophenyl-*p*-phenylenediamine, like the diazoimides containing arylsulphonyl groups, was precipitated from the solution of the corresponding diazonium salt on the addition of sodium acetate. 2 : 4-*Dinitrophenyl*-p-*phenylenediazoimine* (VIII) was not precipitated from a solution of 2 : 4-*dinitrophenyl*-p-*aminobenzenediazonium chloride* by sodium acetate, but only after the addition of potassium hydrogen carbonate. Even the bicarbonate did not determine the precipitation of 4-*nitrophenyl*-p-*phenylenediazoimine* and 2-*nitrophenyl*-*o*-*phenylenediazoimine* (IX), these substances being only deposited on the introduction of aqueous ammonia. In this respect, these isomeric diazoimines resemble phenyl-*p*-phenylenediazoimine (X).

A comparison of the results described below with those formerly obtained by Hantzsch (*loc. cit.*) with phenyl-*p*-phenylenediamine, and by the authors with the arylsulphonyl-*p*-diamides, is shown in the diagram on page 606, where, on the left, are indicated the acids corresponding with the substituents of the amino-groups of the para diamines and their diazonium salts. The first two compounds in this vertical column are benzenesulphonic and picric acids, two substances which are comparable in acidic strength, and from the latter downwards there is a gradual diminution in acidity due to the successive elimination of nitro-groups which corresponds with a gradual decrease in the stability of the diazoimino-derivatives.

The diazoimide (VI) and the diazoimine (VII) exhibit the same degree of stability, but from the latter to the diazoimine (X) there is a gradual falling-off in this respect. However, in spite of the decomposable nature of the less nitrated members of the series, it was found possible to show that they all possess the same general chemical properties, of which the two most characteristic are (1) reconversion into the original diazonium salt, by cold mineral acid; (2) additive combination with β-naphthol to form azo-derivatives. Hantzsch's phenyl-*p*-phenylenediazoimine was re-examined from this point of view, and found to regenerate the diazonium chloride with hydrochloric acid at −12°, and to combine additively with β-naphthol in the presence of pyridine.

In this, as in former communications, the authors have retained



(VI.)

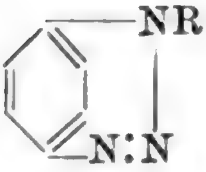
(VII.)

(VIII.)

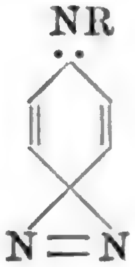
(IX.)

(X.)

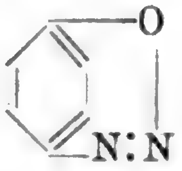
the cyclic diazoimino-formulation (XI) for these diazoimines and diazoimides in preference to the quinonoid configuration (XII),



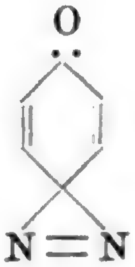
(XI.)



(XII.)



(XIII.)



(XIV.)

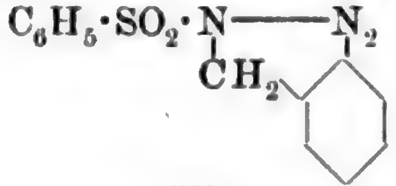
not because, in the authors' opinion, the latter structure is absolutely inadmissible, but owing to the circumstance that the evidence obtained in the course of their experiments points, on the whole, to the diazoimide constitution as offering the simplest explanation of the production and properties of these compounds.

The arguments in favour of each formula may be summarised as follows:

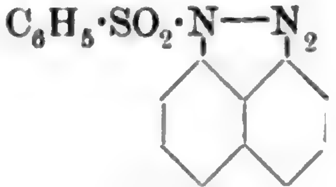
Quinonoid Structure.—1. The yellow colour of these *p*-diazoimides and their sensitiveness to light.

2. The marked contrast between the very reactive para-diazoimides and their isomerides, the inert ortho-diazoimides, points to an essential constitutional difference, incompatible with the similarity of structure shown by formulæ (III) and (XI).

3. The absence of colour in ω-benzenesulphonyl-*o*-benzylenediazoimide (XV),



(XV.)



(XVI.)

a compound in which the quinonoid arrangement is impossible, but which in all its chemical properties resembles the yellow para-diazoimides (Trans., 1906, **89**, 1162).

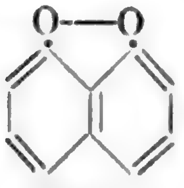
Diazoimino-structure.—1. The colour of the *p*-diazoimides is not incompatible with the presence in their molecule of the group

$$\mathrm{R{-}N_2{\cdot}NR'{-}},$$

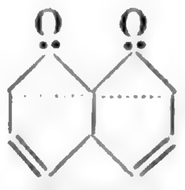
where R and R′ are aromatic residues, for this arrangement is present in the similarly coloured diazoamino-compounds, which also resemble the diazoimides in other respects.

2. The constitution of the ortho-diazoimides stands in want of revision, and therefore affords no trustworthy guide to the cause of the observed differences between the two series of ortho- and para-diazoimides. Even supposing the two series to have the same arrangement of nitrogen atoms, yet the circumstance that, in the para-compounds, these atoms form part of a seven-membered ring, but are, in the ortho-series, included in a five-membered ring, would suffice to account for the great difference in stability of these two types of diazoimides.

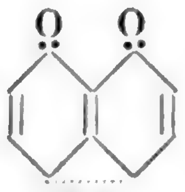
3. The existence of a yellow peri-diazoimide (XVI), similar in all respects to the para-diazoimides, renders the hypothesis of a quinonoid structure for the latter quite unnecessary, for not only has peri-naphthaquinone not been prepared, but even if it were known it is difficult to see how it could be formulated otherwise than as a peroxide (XVII):



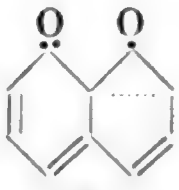
(XVII.)



(XVIII.)



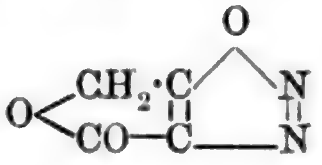
(XIX.



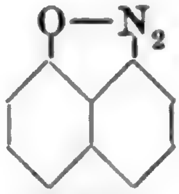
(XX.)

The formulation as a diketone, even when effected with the least amount of rearrangement of the valencies, would lead to the assumption of a five-membered ring as in the formula (XVIII), or of three-membered rings as in formulæ (XIX) and (XX). It is highly improbable that any linking up of carbon atoms occurs in the formation of the peri-diazoimide (XVI), as this substance is readily reconverted into an ordinary naphthalenediazonium salt by the agency of cold acids.

The arguments stated for and against the quinonoid structure of diazoimides apply with equal force to the question of the constitution of the closely allied diazo-oxides. These substances were formerly formulated as cyclic diazo-oxides (XIII), but recently it has become customary to represent them as quinonediazides (XIV). This change of opinion appears to be based on Wolff's observation (*Annalen*, 1900, **312**, 126), that diazotetronic anhydride, which he formulates as a diazo-oxide (XXI),



(XXI.)



(XXII.)

differs from the aromatic diazo-oxides in colour and several other properties, and also to some extent on the fact that the stable colourless *o*-diazosulphides (Jacobson, *Annalen, loc. cit.*) are markedly dissimilar from the *o*- and *p*-diazo-oxides. It is doubtful whether this evidence is sufficiently relevant to justify the replacement of the cyclic formula by a quinonoid configuration, which could not, for the above-mentioned reasons, be extended to the closely-related peri-diazo-oxides (XXII), obtained from 8-amino-α-naphthol and its derivatives (D.R.-P. 55404, 62289, 81282, and 82900).

EXPERIMENTAL.

2 : 4 : 6-*Trinitrophenyl*-p-*phenylenediamine* (*Picryl*-p-*phenylenediamine*), $C_6H_2(NO_2)_3{\cdot}NH{\cdot}C_6H_4{\cdot}NH_2$.

This base, which was first obtained by Wedekind (*Ber.*, 1900, **33**, 435), may be readily prepared by heating together for a few hours in dry toluene a mixture of *p*-phenylenediamine (9 grams), picryl chloride (13 grams), and anhydrous sodium acetate (6 grams). After evaporating off the toluene, the crystalline product is washed with warm alcohol and recrystallised from ethyl acetate, from which solvent it separates in lustrous, black prisms melting at 185—187°. Picryl-*p*-phenylenediamine crystallises also from amyl alcohol or glacial acetic acid, and separates either in dark red or almost black prisms ; it has basic properties, and dissolves in strong hydrochloric acid to form a sparingly soluble hydrochloride.

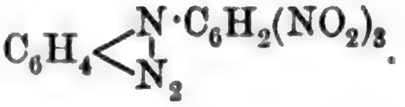
When the foregoing preparation is carried out with molecular proportions of the diamine and picryl chloride, the picryl-*p*-phenylenediamine is found to be contaminated with a non-basic substance insoluble in ethyl acetate, amyl acetate, glacial acetic acid, or toluene. This by-product, when crystallised from nitrobenzene, separated as a red, crystalline powder, which dissolved in aqueous alkalis and did not melt below 260° :

0·1972 gave 36·2 c.c. nitrogen at 19° and 760 mm. N = 21·11.

$C_{18}H_{10}O_{12}N_8$ requires N = 21·13 per cent.

This compound is therefore *bis*-2 : 4 : 6-*trinitrophenyl*-p-*phenylenediamine* (s-*dipicryl*-p-*phenylenediamine*).

2 : 4 : 6-*Trinitrophenyl*-p-*phenylenediazoimine*,



$$C_6H_4{<}\begin{matrix}N\cdot C_6H_2(NO_2)_3\\ |\\ N_2\end{matrix}.$$

Picryl-*p*-phenylenediamine is not readily diazotised, as, even in the presence of excess of mineral acid, the solution of its diazonium chloride froths considerably, and soon deposits a brownish-red substance. In order, therefore, to obtain the diazoimine, the freshly prepared solution of the diazo-salt was filtered into aqueous sodium acetate, and the red precipitate washed with water and alcohol. When dry, the product dissolved in benzene, and is separated on the addition of light petroleum in clusters of brownish-red, diamond-shaped aggregates. The substance exploded at 120—130°, emitting clouds of black smoke :

0·1930 gave 42·6 c.c. nitrogen at 19° and 763 mm. N = 25·47.

0·4148 „ 0·6694 CO_2 and 0·0895 H_2O. C = 44·01 ; H = 2·39.

$C_{12}H_6O_6N_6$ requires N = 25·47 ; C = 43·63 ; H = 1·81 per cent.

On extracting the crude diazoimine with benzene, a brown residue was left which was not explosive. This substance, which seemed to be identical with the brownish-red by-product formed during diazotisation, was not further examined.

The diazoimine, when intimately mixed with β-naphthol and moistened with dry pyridine, showed very little sign of combination until the mixture was gently warmed, when the formation of azo-compound immediately occurred, and the mass reddened and acquired a green metallic reflex. The product, when freed from excess of β-naphthol by extraction with warm alcohol, was dissolved in ethyl acetate or toluene and precipitated from the latter solvent by alcohol. 2 : 4 : 6-*Trinitrophenyl*-p-*aminobenzeneazo*-β-*naphthol*,

$$C_6H_2(NO_2)_3\cdot NH\cdot C_6H_4\cdot N_2\cdot C_{10}H_6\cdot OH,$$

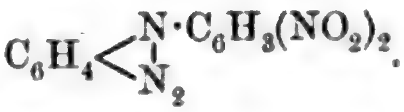
was thus obtained as a crystalline, reddish-brown powder, blackening at 190°, and melting at 217°:

0·1842 gave 27·8 c.c. nitrogen at 19° and 759 mm. N = 17·35.

$C_{22}H_{14}O_7N_6$ requires N = 17·72 per cent.

This azo-β-naphthol cannot be prepared by adding 2 : 4 : 6-trinitrophenyl-*p*-aminobenzenediazonium chloride to alkaline β-naphthol, for the product thus obtained contained only 10·58 per cent. of nitrogen, was very soluble in alcohol, and did not melt below 260°.

2 : 4-*Dinitrophenyl*-p-*phenylenediazoimine*,



$$C_6H_4<\begin{array}{l}N\cdot C_6H_3(NO_2)_2\\ \,|\\ N_2\end{array}.$$

2 : 4-Dinitrophenyl-*p*-phenylenediamine, prepared according to Nietzki and Ernst's method (*Ber.*, 1890, **23**, 1852) by boiling together molecular proportions of chloro-2 : 4-dinitrobenzene and *p*-phenylenediamine in alcoholic solution containing anhydrous sodium acetate, was crystallised from benzene, when it separated first in flakes, which redissolved as the solution cooled, and then in lustrous, red crystals, which melted at 190°, and not at 177° as stated by the above authors.

2 : 4-*Dinitrophenyl*-p-*aminobenzenediazonium chloride*,

$$C_6H_3(NO_2)_2\cdot NH\cdot C_6H_4\cdot N_2\cdot Cl,H_2O,$$

was obtained by diazotising the somewhat insoluble red hydrochloride of the preceding base, when a clear solution was obtained, which yielded a mass of transparent, golden-yellow needles; these were recrystallised from very dilute hydrochloric acid, washed successively with dilute hydrochloric acid, alcohol, and ether, and finally dried over quicklime:

0·2380 gave 0·0974 AgCl. Cl = 10·13.

$C_{12}H_8O_4N_5Cl,H_2O$ requires Cl = 10 40 per cent.

This salt seems to undergo hydrolytic decomposition when treated with water.

2 : 4-*Dinitrophenyl*-p-*aminobenzeneazo*-β-*naphthol*,

$$C_6H_3(NO_2)_2\cdot NH\cdot C_6H_4\cdot N_2\cdot C_{10}H_6\cdot OH,$$

was obtained as a scarlet precipitate on pouring a solution of the preceding diazo-salt into alkaline β-naphthol. It was somewhat soluble in benzene or toluene, but separated from alcohol as a red, microcrystalline powder melting at 230°:

0·2222 gave 32·8 c.c. nitrogen at 20° and 758 mm. N = 16·84.

$C_{22}H_{15}O_5N_5$ requires N = 16·31 per cent.

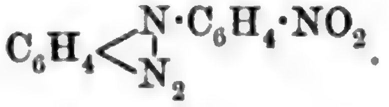
Addition of sodium acetate to the clear yellow solution of the diazo-salt did not produce any precipitate, and accordingly after three hours potassium hydrogen carbonate was introduced, when a red, crystalline substance was deposited, the precipitation being then complete. These crystals, which had a velvety texture, exploded on warming at 110—115°:

0·1548 gave 32·8 c.c. nitrogen at 19° and 762 mm. N = 24·44.
0·1716 „ 0·3170 CO_2 and 0·0484 H_2O. C = 50·38; H = 3·13.
$C_{12}H_7O_4N_5$ requires N = 24·56; C = 50·52; H = 2·45 per cent.

2 : 4-*Dinitrophenyl*-p-*phenylenediazoimine* dissolves slightly in alcohol and may be recrystallised from benzene, but not without partial decomposition; it darkens rapidly on exposure to light.

A mixture of this diazoimine and β-naphthol, when moistened with pyridine and gently warmed, immediately yielded the azo-derivative. This product was freed from β-naphthol with aqueous caustic soda and then crystallised from toluene, when it separated in lustrous, transparent, red prisms, melting at 233—235°, and giving practically the same melting point when mixed with the azo-β-naphthol obtained from the diazo-salt. Both preparations developed a deep purple coloration with concentrated sulphuric acid, the liquid assuming a blue tint on gradual dilution with ice-cold water.

4-*Nitrophenyl*-p-*phenylenediazoimide*,



$$C_6H_4<\begin{matrix}N\cdot C_6H_4\cdot NO_2\\ |\\ N_2\end{matrix}.$$

The method described by Bandrowski (*Chem. Centr.*, 1900, **71**, 852) was followed in preparing 4-nitrophenyl-*p*-phenylenediamine; 8 grams of 4-bromonitrobenzene, 6 grams of *p*-phenylenediamine (1·5 molecules), and 4 grams of fused sodium acetate were intimately mixed, moistened with 10 c.c. of alcohol, and heated in a sealed tube for eight hours at 160—170°. The product was thoroughly extracted with ether, and the soluble substance left, after removing the solvent, was washed with hot water, and then extracted with hot dilute hydrochloric acid. The base liberated from this solution crystallised from benzene in red leaflets and melted at 205°; the temperature formerly given for this melting point was 211—212°. When diazotised, the sparingly soluble yellow hydrochloride of this base furnished a solution in which neither sodium acetate nor potassium hydrogen carbonate caused a precipitate. The addition of ammonia, however, determined the formation of an insoluble diazoimine, which separated in micaceous, red crystals having a coppery lustre. The dry substance exploded when rubbed, and on warming to 60—65° was projected violently from the melting-point tube:

0·1792 gave 34·6 c.c. nitrogen at 17° and 762 mm. N = 22·48.
0·1456 „ 0·3210 CO_2 and 0·0480 H_2O. C = 60·11; H = 3·66.
$C_{12}H_8O_2N_4$ requires N = 23·33; C = 60·00; H = 3·33 per cent.

The diazoimine readily combined with β-naphthol in the presence of pyridine, the azo-derivative crystallised from benzene in long, black prisms:

0·1830 gave 22·4 c.c. nitrogen at 18° and 774 mm. N = 14·40.

$C_{22}H_{16}O_3N_4$ requires N = 14·58 per cent.

4-*Nitrophenyl*-p-*aminobenzeneazo-β-naphthol*,

$NO_2 \cdot C_6H_4 \cdot NH \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot OH$,

was also prepared from the diazo-salt and β-naphthol. Both preparations melted at 266° and developed with concentrated sulphuric acid a bright crimson coloration, which assumed a violet tint as the acid became diluted.

2-*Nitrophenyl*-p-*phenylenediazoimine.*

2-Nitrophenyl-*p*-phenylenediamine was prepared in the same way as the preceding diamine from 2-bromonitrobenzene and *p*-phenylenediamine. The mode of extraction was similar, and the base was finally obtained as a reddish-black, crystalline product (m. p. 105—106°) with a green, metallic reflex.

The sparingly soluble hydrochloride of 2-nitrophenyl-*p*-phenylenediamine when diazotised yielded a solution of the diazo-salt from which neither sodium acetate nor potassium hydrogen carbonate precipitated the diazoimine; this compound was, however, deposited as a scarlet precipitate when the well-cooled ammonia is added to the sodium acetate solution. This diazoimine was even more unstable than its isomeride; it darkened at 30°, and exploded at 85—90°. The dry substance also exploded when gently rubbed on a hard surface:

0·1880 gave 0·4132 CO_2 and 0·0670 H_2O. C = 59·94; H = 3·96.

0·1802 „ 33·0 c.c. nitrogen at 18° and 773 mm. N = 21·55.

$C_{12}H_8O_2N_4$ requires C = 60·00; H = 3·33; N = 23·33 per cent.

2-*Nitrophenyl*-p-*phenylenediazoimine* was precipitated in the amorphous condition and could not be crystallised, as it underwent decomposition even when kept dry at the ordinary temperature. In these circumstances, it gradually lost in weight owing to the elimination of nitrogen; the rapidity with which this change occurred accounts for the low results obtained on estimating this element.

A freshly prepared specimen of the diazoimine was rapidly dried on porous tile, and left in contact with β-naphthol and pyridine at the ordinary temperature. The product was extracted with alcohol, and the dark residue dissolved in benzene; this solution, on the addition of light petroleum, yielded a brick-red azo-derivative, which blackened at 130°, and melted at 158—160°:

0·1136 gave 14·5 c.c. nitrogen at 18° and 758 mm. N = 14·70.

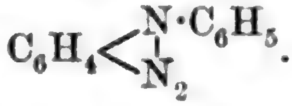
$C_{22}H_{16}O_3N_4$ requires N = 14·58 per cent.

2-*Nitrophenyl*-p-*aminobenzeneazo*-β-*naphthol*,

$$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH,$$

can also be prepared by the direct interaction of 2-nitrophenyl-*p*-aminobenzenediazonium chloride and alkaline β-naphthol. With concentrated sulphuric acid, the azo-compound developed a crimson coloration, which changed to deep blue as the solution absorbed moisture. In the dry state, the particles of this azo-β-naphthol were found to be highly electrified.

Phenyl-p-*phenylenediazoimine* (*Ber*., 1902, **35**, 888),



$$C_6H_4{<}\begin{matrix}N{\cdot}C_6H_5\\ |\\ N_2\end{matrix}.$$

This diazoimine was prepared by diazotising phenyl-*p*-phenylenediamine hydrochloride with sodium nitrite and excess of well-cooled dilute hydrochloric acid, and treating the clear solution thus obtained with cold dilute ammonia. The brownish-yellow precipitate was collected, dried on cooled tiles, and subjected to the following tests.

One portion was made into a paste with ice-cold water and treated with cooled hydrochloric acid (1, strong acid; 2, water), the reagents being cooled in a freezing mixture. The diazoimine dissolved almost entirely, and the filtered solution was shown to contain the diazonium salt by adding one portion to ammonia, when the diazoimine was regenerated, and also by introducing another portion into alkaline β-naphthol, when *phenyl*-p-*aminobenzeneazo*-β-*naphthol*,

$$C_6H_5{\cdot}NH{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH,$$

was obtained. This compound crystallised from benzene or toluene in brownish-black leaflets melting at 168—170°. It was also produced by mixing the diazoimine with β-naphthol and pyridine, when lustrous, black leaflets were obtained. The azo-β-naphthol, when dissolved in alcohol and precipitated by the addition of water, was deposited as a black, crystalline powder with a metallic lustre:

0·1456 gave 14·4 c.c. nitrogen at 16° and 764 mm. N = 11·60.

$C_{22}H_{17}ON_3$ requires N = 12·38 per cent.

The azo-β-naphthol prepared by either of the foregoing methods developed with concentrated sulphuric acid a bright cherry-red coloration, which changed to blue as the solution absorbed moisture from the atmosphere.

The authors desire to express their thanks to the Government Grant Committee of the Royal Society for a grant which has partly defrayed the expenses of this investigation.

ROYAL COLLEGE OF SCIENCE, LONDON.
SOUTH KENSINGTON, S.W.

LVI.—*A Study of the Diazo-reaction in the Diphenyl Series.*

By Gilbert T. Morgan and Frances M. G. Micklethwait.

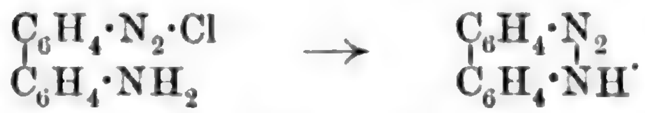
Although there is a general similarity between the homonuclear aromatic para-diamines such as *p*-phenylenediamine and the heteronuclear bases of the benzidine type, yet the fact that in the latter series the amino-groups are situated in different rings leads to certain peculiarities in the chemical reactions of the diphenyl bases.

When *p*-phenylenediamine and benzidine are treated with sufficient sodium nitrite in the presence of excess of mineral acid, they are both converted into bisdiazonium salts, but in the case of the latter base a modification of the works process of diazotisation has been found to lead to the production of the intermediate aminodiazonium salt, $NH_3Cl \cdot C_6H_4 \cdot C_6H_4 \cdot N_2Cl$ (Farbenfabriken vorm. F. Bayer & Co., D.R.-P. 51576, and Badische Anilin- & Soda-Fabrik, D.R.-P. 52661). Taüber, who throws some doubt on this reaction, has shown, nevertheless, that the intermediate compound results from the interaction of the hydrochlorides of fully diazotised benzidine and the undiazotised base, the yield of the aminodiazonium salt being approximately 80—90 per cent. (*Ber.*, 1894, **27**, 2628).

Fully diazotised benzidine has the peculiar property of combining rapidly with one molecular proportion of a phenol or reactive amine, forming an intermediate substance still containing a diazo-group, which couples slowly with a second molecule of the phenol or amine. The manufacture of Congo red furnishes an excellent example of this combination in two stages.

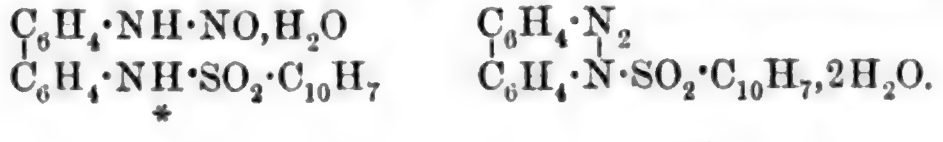
On the theoretical side, these results have had some bearing on the speculations relating to the steric relationship of the two phenyl groups in benzidine, the current opinion being that the two nuclei are doubled on themselves so as to render the amino-groups contiguous. This proximity would lead to some steric hindrance, as in the foregoing azo-condensation, and would also account for the manner in which the bisdiazonium chloride can be decomposed in two stages on treatment with absolute alcohol (*Ber.*, 1898, **31**, 479).

This view as to the close proximity of the amino-groups receives further confirmation from the fact mentioned in the patent D.R.-P. 51576, and again referred to by Vaubel and Scheuer (*Zeitsch. Farb. Ind.*, 1906, **5**, 61), that the above-mentioned aminodiazo-salt, on treatment with sodium acetate, gives rise to a condensation product which is regarded as being a diazoimine:



$$\begin{array}{l} C_6H_4\cdot N_2\cdot Cl \\ | \\ C_6H_4\cdot NH_2 \end{array} \longrightarrow \begin{array}{l} C_6H_4\cdot N_2 \\ |\qquad\quad | \\ C_6H_4\cdot NH \end{array}.$$

Diazoimines of this type have not hitherto been obtained from *p*-phenylenediamine and its homologues, although the authors of this communication have obtained a stable series of para-diazoimides from the arylsulphonyl-*p*-phenylenediamines (Trans., 1905, **87**, 73, 921; 1906, **89**, 4, 1158, and preceding paper). It was therefore to be expected that the arylsulphonylbenzidines would yield such diazo-anhydrides even more readily than benzidine itself. This, however, is not the case. Benzenesulphonylbenzidine, when successively diazotised and treated with sodium acetate, furnishes a well-defined crystalline product which, although possessing some of the properties of a *p*-diazoimide, nevertheless contains two molecules of water which are so tenaciously held that the substance decomposes before the elimination of water is complete (Trans., 1907, **91**, 1506). This result was so unexpected that another base of the same type was examined in order to ascertain whether the reaction is in any way exceptional. *Naphthalene-β-sulphonylbenzidine* was chosen for this purpose, and experiment showed that the new base furnished a dark brown, crystalline, dihydrated compound of precisely similar type to that obtained from the other base. Two views may be held concerning these compounds, according to which they may be regarded as either monohydrated primary nitroamines (I) or dihydrated diazoimides (II):

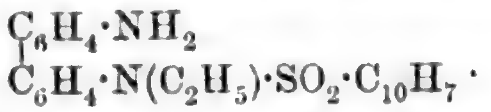


$$\begin{array}{l} C_6H_4\cdot NH\cdot NO,H_2O \\ | \\ C_6H_4\cdot \underset{*}{N}H\cdot SO_2\cdot C_{10}H_7 \end{array} \qquad \begin{array}{l} C_6H_4\cdot N_2 \\ |\qquad\quad | \\ C_6H_4\cdot N\cdot SO_2\cdot C_{10}H_7,2H_2O. \end{array}$$

I. II.

The first of these formulations accounts for the fact that the substances dissolve in aqueous alkali, and also brings the compounds into line with other nitrosoamine derivatives which are sometimes found to contain one molecule of water (Schraube and Schmidt, *Ber.*, 1894, **27**, 520).

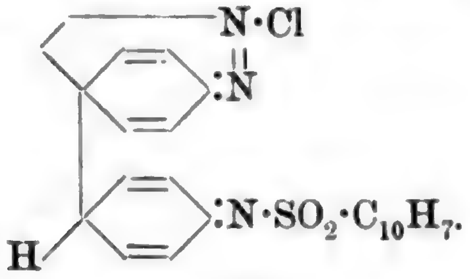
The second formula indicates the close similarity between these compounds and the para-diazoimides, and it also explains the non-production of a similar compound when the marked hydrogen (*) is replaced by an alkyl group as in as-*naphthalene-β-sulphonylethylbenzidine*,



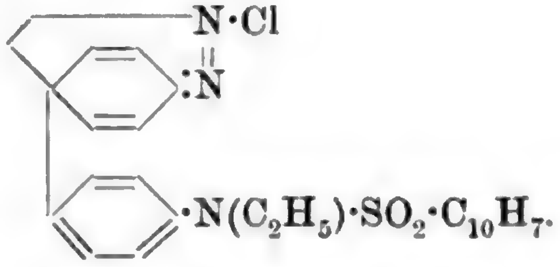
$$\begin{array}{l} C_6H_4\cdot NH_2 \\ | \\ C_6H_4\cdot N(C_2H_5)\cdot SO_2\cdot C_{10}H_7 \end{array}.$$

A similar combination of water and a diazo-anhydride has been observed in the case of *p*-phenylenediazo-oxide (from *p*-diazophenol), this substance separating with $4H_2O$ (Hantzsch and Davidson, *Ber.*, 1896, **29**, 1522).

The diazonium salts of naphthalene-β-sulphonylbenzidine are all distinctly coloured substances, being usually orange or yellow, but those of *as*-naphthalene-β-sulphonylethylbenzidine are much less coloured, having only a pale yellow tint, the substitution of hydrogen by ethyl in the arylsulphonic group diminishing the colour to a marked extent without entirely removing it. It seems, therefore, very unlikely that the diazonium complexes in the two series are differently constituted, and the difference in the intensity of colour may be referred to the existence of two quinonoid nuclei in the more coloured salts (III), whereas only one of these groups can exist in the case of the diazonium salts (IV) of the alkylated base:



(III.)



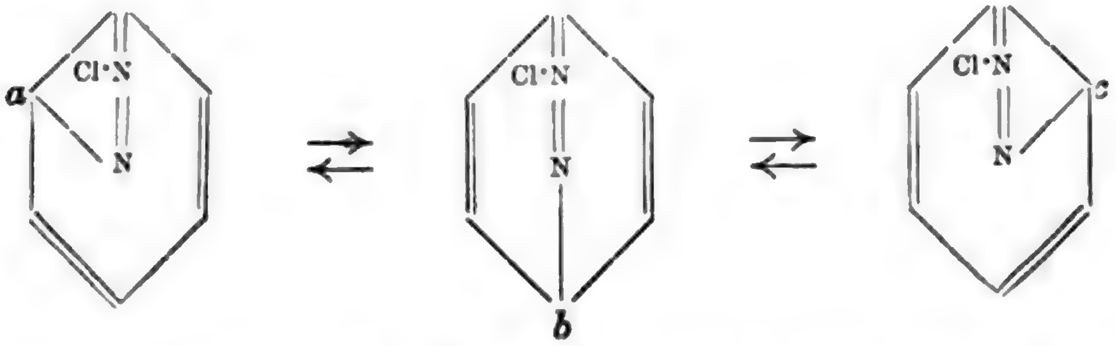
(IV.)

In the foregoing formulæ, the para-quinonoid formula advocated by Cain is taken to represent the constitution of these diazonium salts. It should, however, be borne in mind that an ortho-quinonoid configuration for these substances is not inadmissible (Trans., 1907, **91**, 1315).

Exception has been taken to these quinonoid formulæ on the ground that they represent one of the diazo-nitrogens as being definitely attached to a carbon atom in either a para- or an ortho-position, an arrangement which on reduction should lead, in certain circumstances, to the production of either para- or ortho-diamines. Diazonium salts have not, however, been found to yield these diamines on reduction, and it seems, therefore, improbable that this linking of diazo-nitrogen to para- or ortho-carbon atoms is quite of the ordinary kind. On the other hand, it has long been supposed that another position in the ring is in some way involved in the diazonium complex. This view, which was originally held by Griess (*Annalen*, 1866, **137**, 47), accords with the most salient fact known about diazonium salts, namely, that these substances are only obtainable from amines containing the unsaturated aromatic nuclei, and not from bases containing fully hydrogenated rings.

It is, therefore, justifiable to suppose that the residual affinities of the benzene nucleus—indicated by three double linkings in Kekulé's formula for this hydrocarbon—are in some way associated with the diazonium complex. However, until Cain put forward his para-quinonoid formula, this association of the latent valency of the benzene ring with the diazonium group had not been indicated in any of the configurations ascribed to diazo-salts.

The authors now suggest that these static ortho- and para-quinonoid formulæ represent successive phases in the existence of a diazonium salt, the constitution of which is continually changing from one to the other of these configurations in the manner indicated in the following diagram:



The third valency of the non-saline triadic diazo-nitrogen is directed successively to the carbon atoms marked *a*, *b*, and *c*, but is not held continuously by any one of them. This mode of expressing the structure of the diazonium salt retains the advantages claimed by Cain for his para-quinonoid formula, and in addition enables one to account for the behaviour of these compounds on reduction.*

In an ever-increasing number of instances, it becomes impossible to represent satisfactorily the reactions of compounds by static graphical formulæ, and in these cases it is apparent that the valency directions undergo certain rhythmical variations such as those symbolised in the foregoing dynamic formula proposed for diazonium salts.

EXPERIMENTAL.

Naphthalene-β-sulphonyl-p-*nitroaminodiphenyl*, $C_{10}H_7{\cdot}SO_2{\cdot}NH{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NO_2$.

pp-Dinitrodiphenyl was prepared according to Willstätter's method and reduced with sulphuretted hydrogen (*Ber.*, 1906, **39**, 3478). The resulting *p*-nitroaminodiphenyl was condensed in dry pyridine with a slight excess of naphthalene-β-sulphonic chloride, and the product, after extraction with aqueous caustic soda and reprecipitation with dilute acetic acid, was crystallised from alcohol, when it separated in reddish-brown, serrated crystals having a bluish reflex and melting at 164—165°:

---

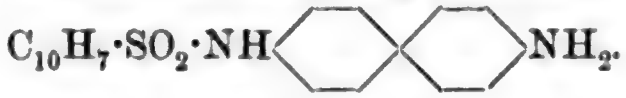
* Orton and Reed have shown (Trans., 1907, **91**, 1561) that, with the diazo-salts of the highly halogenated anilines, the replacement of halogen by hydroxyl occurs to a much greater extent in the ortho- than in the para-position, and they put this result forward as an argument against the para-quinonoid formula. At the same time, however, they suggest that the assumption of an alternation of para- and ortho-quinonoid configurations would be more in harmony with their results

0·3696 gave 23·6 c.c. nitrogen at 19° and 762 mm. N = 7·36.

$C_{22}H_{16}O_4N_2S$ requires N = 6·93 per cent.

The sodium derivative of this nitro-compound crystallised in orange-yellow plates, which were only sparingly soluble in cold water.

Naphthalene-β-sulphonylbenzidine,



This base was prepared by reducing the preceding compound with iron and dilute hydrochloric acid, the mixture being boiled for many hours in order to complete the reduction. Finally, the mixture was rendered alkaline with sodium carbonate, and the base obtained from the filtrate as a colourless, gelatinous mass which, when crystallised from benzene, separated in clusters of fibrous, colourless needles melting at 185—186°. The reduction may also be effected with tin and hydrochloric acid:

0·1754 gave 10·8 c.c. nitrogen at 19° and 761 mm. N = 7·10.

$C_{22}H_{18}O_2N_2S$ requires N = 7·48 per cent.

An attempt was made to prepare this base by the interaction of benzidine and naphthalene-β-sulphonic chloride. The required product was only obtained when benzidine dissolved in cold, dry pyridine was treated very slowly with finely-powdered naphthalene-β-sulphonic chloride (1 mol.). After some hours, the mixture was gently warmed on the steam bath, then poured on to ice, and extracted successively with dilute hydrochloric acid and water. A benzene extract of the dried residue yielded a small amount of impure naphthalene-β-sulphonylbenzidine which, after repeated crystallisation from this solvent, melted at 185—186° and did not depress the melting point of the preceding preparation:

0·1698 gave 0·1074 $BaSO_4$. S = 8·68.
0·0986 „ 6·2 c.c. nitrogen at 19° and 754 mm. N = 7·17.

$C_{22}H_{18}O_2N_2S$ requires S = 8·55; N = 7·48 per cent.

Naphthalene-β-sulphonylaminodiphenyldiazonium Chloride,

$C_{10}H_7{\cdot}SO_2{\cdot}NH{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}N_2Cl$.

The addition of excess of amyl nitrite to an alcoholic solution of naphthalene-β-sulphonylbenzidine produced a deep-red coloration which was not appreciably changed by the addition of alcoholic hydrochloric acid. The filtered solution, when treated with excess of ether, furnished the yellow, crystalline diazonium chloride:

0·0580 gave 5·2 c.c. nitrogen at 19° and 760 mm. N = 10·30.
0·2476 „ 0·0802 AgCl. Cl = 8·02.
$C_{22}H_{16}O_2N_3ClS$ requires N = 9·97 ; Cl = 8·42 per cent.

This salt dissolved in acidified water to a clear, yellow solution; it decomposed and charred at 140—145°:

The *diazonium bromide*, $C_{10}H_7\cdot SO_2\cdot NH\cdot C_6H_4\cdot C_6H_4\cdot N_2Br$, an ill-defined yellow salt, decomposed violently at 120—124°:

0·1672 gave 12·5 c.c. nitrogen at 18° and 769 mm. N = 8·75.
$C_{22}H_{16}O_2N_3BrS$ requires N = 9·01 per cent.

The *diazonium sulphate*, $C_{10}H_7\cdot SO_2\cdot NH\cdot C_6H_4\cdot C_6H_4\cdot N_2\cdot HSO_4$, was obtained in yellow needles when amyl nitrite, sulphuric acid, and ether were successively added to a solution of the base in cold glacial acetic acid. This salt decomposed at about 125°:

0·1426 gave 10·5 c.c. nitrogen at 17° and 769 mm. N = 8·64.
0·1340 „ gave 0·1364 $BaSO_4$. S = 13·97.
$C_{22}H_{16}O_2N_3S,HSO_4$ requires N = 8·69 ; S = 13·25 per cent.

The Brown, Crystalline Product

The foregoing diazonium chloride, when treated with aqueous sodium acetate, yielded a dark-brown, crystalline substance almost insoluble in cold water or alcohol. When thoroughly washed with these solvents and dried over sulphuric acid until of constant weight, the substance gave the following analytical data, a different preparation being used in each analysis:

0·2745 gave 0·6299 CO_2 and 0·1146 H_2O. C = 62·57 ; H = 4·64.
0·1614 „ 0·3723 CO_2 and 0·0698 H_2O. C = 62·90 ; H = 4·80.
0·1691 „ 14·0 c.c. nitrogen at 19° and 764 mm. N = 9·57.
0·2647 „ 0·1500 $BaSO_4$. S = 7·78.
$C_{22}H_{15}O_2N_3S,2H_2O$ requires C = 62·70 ; H = 4·71 ; N = 9·97 ; S = 7·60 per cent.

This compound reacts with cold concentrated hydrochloric acid, regenerating the diazonium chloride; it dissolved in aqueous caustic soda to a brown solution, from which dilute acetic acid reprecipitated the original compound. The reprecipitated substance had a reddish tint, but slowly assumed the chocolate-brown colour. Attempts to eliminate water without decomposing the substance were unsuccessful; it appeared to lose water and nitrogen simultaneously, becoming yellow at 100°, and darkening and softening at about 130°.

When mixed with dry β-naphthol, the brown compound gave no reaction even on warming, but the addition of a few drops of dry pyridine at once induced combination. The *azo-β-naphthol* thus obtained was scarcely soluble in cold alcohol, but separated from its boiling solution in this solvent as a dark-red, crystalline powder melting at 200—201°.

Naphthalene-β-sulphonylnitroethylaminodiphenyl, $C_{10}H_7 \cdot SO_2 \cdot N(C_2H_5) \cdot C_6H_4 \cdot C_6H_4 \cdot NO_2$.

This compound was produced by the interaction of naphthalene-β-sulphonylnitroaminodiphenyl, ethyl iodide, and alcoholic potash. The reaction was almost complete, and the product, when freed from substances soluble in alkali, was crystallised from alcohol, when it separated in transparent, orange-yellow needles melting at 152—153°:

0·1770 gave 10·0 c.c. nitrogen at 19° and 761 mm. N = 6·50.

$C_{24}H_{20}O_4N_2S$ requires N = 6·48 per cent.

as-*Naphthalene-β-sulphonylethylbenzidine*, $C_{10}H_7 \cdot SO_2 \cdot N(C_2H_5) \cdot C_6H_4 \cdot C_6H_4 \cdot NH_2$.

The preceding nitro-compound, when boiled with iron and dilute hydrochloric acid for eight hours, was reduced to *as*-naphthalene-β-sulphonylethylbenzidine, which separated from its benzene solution on the addition of light petroleum as a brown, crystalline powder melting at 165—166°:

0·2401 gave 15·0 c.c. nitrogen at 18° and 760 mm. N = 7·21.
0·2360 ,, 0·1518 $BaSO_4$. S = 8·83.

$C_{24}H_{22}O_2N_2S$ requires N = 6·96 ; S = 8·00 per cent.

as-*Naphthalene-β-sulphonylethyldiphenyldiazonium Chloride*, $C_{10}H_7 \cdot SO_2 \cdot N(C_2H_5) \cdot C_6H_4 \cdot C_6H_4 \cdot N_2Cl$.

This salt was obtained in clusters of pale yellow needles by adding successively alcoholic hydrochloric acid and ether to a mixture of the base and amyl nitrite in alcohol.

0·2110 gave 16·5 c.c. nitrogen at 18° and 769 mm. N = 9·15.
0·1192 ,, 0·0364 AgCl. Cl = 7·56.

$C_{24}H_{20}O_2N_3ClS$ requires N = 9·34 ; Cl = 7·89 per cent.

This diazonium chloride, when triturated with concentrated aqueous sodium acetate, furnished a slimy precipitate which dissolved in water to a red solution. There was no evidence of the formation of an insoluble, crystalline product analogous to that obtained from the diazo-chloride of naphthalene-β-sulphonylbenzidine.

The *diazonium bromide*, $C_{10}H_7 \cdot SO_2 \cdot N(C_2H_5) \cdot C_6H_4 \cdot C_6H_4 \cdot N_2Br$, prepared in a similar manner to the preceding salt, was obtained in the form of very pale yellow needles:

0·2034 gave 14·6 c.c. nitrogen at 18° and 770 mm. N = 8·41.
0·1771 „ 0·0661 AgBr. Br = 15·87.
$C_{24}H_{20}O_2N_3BrS$ requires N = 8·50 ; Br = 16·19 per cent.

The diazo-chloride decomposed at 116—117°, and the diazo-bromide at 113—116°.

The *diazonium sulphate*, $C_{10}H_7{\cdot}SO_2{\cdot}N(C_2H_5){\cdot}C_6H_4{\cdot}C_6H_4{\cdot}N_2{\cdot}HSO_4$, produced in glacial acetic acid and precipitated by ether, resembled the bromide:

0·1838 gave 12·8 c.c. nitrogen at 19° and 771 mm. N = 8·13.
0·1660 „ 0·1516 $BaSO_4$. S = 12·54.
$C_{24}H_{20}O_2N_3S,HSO_4$ requires N = 8·21 ; S = 12·52 per cent.

The three foregoing diazo-salts furnished an *azo-β-naphthol* insoluble in aqueous alkalis; this substance, which was very soluble in benzene, dissolved sparingly in alcohol, and separated as an ill-defined precipitate melting at 155—157°.

The authors desire to express their thanks to the Government Grant Committee of the Royal Society for a grant which has partly defrayed the expenses of this investigation.

ROYAL COLLEGE OF SCIENCE, LONDON,
SOUTH KENSINGTON, S.W.

LVII.—*The Action of Mustard Oils on the Ethyl Esters of Malonic and Cyanoacetic Acids.*

By SIEGFRIED RUHEMANN.

THE further study of thioxanthoxalanil (Ruhemann, Trans., 1907, **91**, 797), and especially the behaviour of the sodium derivative of its tautomeride towards alkyl iodides, led to results which induced me to undertake the work described in this paper.

Michael (*J. pr. Chem.*, 1887, [ii], **35**, 450) showed that ethyl sodiomalonate readily united with phenylthiocarbimide to yield a product, the formation of which he expressed thus:

$$CHNa(CO_2Et)_2 + C_6H_5{\cdot}NCS = C_6H_5{\cdot}N{:}C(S{\cdot}Na){\cdot}CH(CO_2Et)_2.$$

The sodium compound, by the action of hydrochloric acid, was transformed into the yellow thioanilide of diethyl methanetricarboxylate, $C_6H_5{\cdot}NH{\cdot}CS{\cdot}CH(CO_2Et)_2$.

That the sodium in the additive product is united with the sulphur, follows from the fact that, with benzyl chloride, it yields a benzyl derivative which, on account of the way it decomposes with acids, must have the formula $C_6H_5N{:}C(S{\cdot}CH_2{\cdot}C_6H_5){\cdot}CH(CO_2Et)_2$. From this view as to the constitution of the compound formed by the union of ethyl sodiomalonate with phenylthiocarbimide, it might be expected that the latter would combine with the sodium derivative of monoalkyl malonic esters. In order to test the correctness of this conclusion, ethyl sodiobenzylmalonate was selected, which, accordingly, ought to yield an ester, $C_6H_5{\cdot}N{:}C(SH){\cdot}C(CH_2{\cdot}C_6H_5)(CO_2Et)_2$, isomeric with the benzyl derivative. It was found, however, that this union does not take place, ethyl benzylmalonate remains unaltered, and the mustard oil is transformed into phenylthiourethane,

$$C_6H_5{\cdot}NH{\cdot}CS{\cdot}O{\cdot}C_2H_5.$$

This result would agree with the formula

$$C_6H_5{\cdot}NH{\cdot}C(SNa){:}C(CO_2Et)_2$$

for the additive product of ethyl sodiomalonate with phenylthiocarbimide, but in the absence of other evidence in favour of this view the former mode of representing this reaction is adopted.

The thioanilide of diethyl methanetricarboxylate, on treatment with ammonia, yields the corresponding diamide, whereas by the action of potassium hydroxide at the ordinary temperature the elimination of one molecule of carbon dioxide takes place, as well as hydrolysis. The thioanilide of malonic acid, which is formed on heating below 100°, decomposes into thioacetanilide and carbon dioxide. These changes may be represented thus:

$$C_6H_5{\cdot}NH{\cdot}CS{\cdot}CH(CO_2Et)_2 \longrightarrow C_6H_5{\cdot}NH{\cdot}CS{\cdot}CH_2{\cdot}CO_2H \longrightarrow C_6H_5{\cdot}NH{\cdot}CS{\cdot}CH_3.$$

Michael, in his paper, "On Certain Laws and their Application to Organic Chemistry" (*J. pr. Chem.*, 1899, [ii], **60**, 286), dealt with the action of phenylcarbimide on the sodium derivatives of ethyl malonate and ethyl acetoacetate, and mentioned in a footnote which was noticed after this work was completed that he obtained similar results on using phenylthiocarbimide instead of phenylcarbimide, but a record of the experimental facts was not published.

Phenylthiocarbimide unites with ethyl sodiocyanoacetate in the same manner as with the corresponding compound of malonic acid, and yields the thioanilide of ethyl cyanomalonate. This ester exists in two modifications; the one is colourless and readily changes into the other, which is yellow. The two forms are probably to be represented by the formulæ:

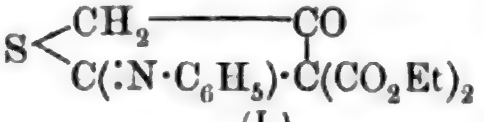
$$C_6H_5{\cdot}NH{\cdot}CS{\cdot}CH(CN){\cdot}CO_2Et \text{ and } C_6H_5{\cdot}N{:}C(SH){\cdot}CH(CN){\cdot}CO_2Et.$$

The thioanilide of ethyl cyanomalonate resembles the former additive product, and, with bases, forms well-defined salts, which in turn react with benzyl chloride to yield the colourless benzyl derivative, $C_6H_5{\cdot}N{:}C(S{\cdot}CH_2{\cdot}C_6H_5){\cdot}CH(CN){\cdot}CO_2Et$.

Of interest is the behaviour of the thioanilides of diethyl methanetricarboxylate and ethyl cyanomalonate towards ethyl chloroacetate. The action of this ester on the sodium derivatives of the thioanilides proceeds, for example, as follows:

$$C_6H_5\cdot N\colon C(S\cdot Na)\cdot CH(CO_2Et)_2 + CH_2Cl\cdot CO_2Et = C_{16}H_{17}O_5NS + C_2H_6O + NaCl,$$

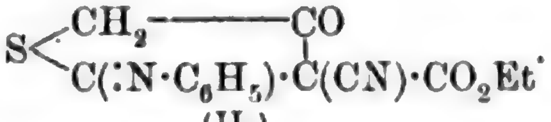
and yellow compounds are also formed. If one accepts Michael's view concerning the manner in which mustard oils unite with ethyl malonate, the above-mentioned substances, according to their formation, may be expressed by the formulæ:



$$\mathrm{S}<\begin{matrix}\mathrm{CH_2}\text{———————}\mathrm{CO}\\ \mathrm{C(\colon N\cdot C_6H_5)\cdot C(CO_2Et)_2}\end{matrix}$$

(I.)

and



$$\mathrm{S}<\begin{matrix}\mathrm{CH_2}\text{———————}\mathrm{CO}\\ \mathrm{C(\colon N\cdot C_6H_5)\cdot C(CN)\cdot CO_2Et}\end{matrix}$$

(II.)

When the compound (I) is heated, it melts at 115—116°, but immediately solidifies, and then does not fuse until 135—136°. This phenomenon may be due to an isomeric change; such a transformation, indeed, is effected by the action of potassium hydroxide, when an isomeride is produced which is colourless, and, on heating, shows a somewhat different behaviour from the yellow modification, for it softens at 105° and only gradually melts at 134°. The yellow condensation product (II), under the influence of alkali, changes in the same way as the former, and yields a colourless isomeride. Experiments, with the view of arriving at an explanation of these phenomena, are in progress, and I hope to publish the results shortly.

EXPERIMENTAL.

Thioanilide of Diethyl Methanetricarboxylate, $C_6H_5\cdot NH\cdot CS\cdot CH(CO_2Et)_2$.

This substance was prepared according to Michael's directions (*loc. cit.*), by mixing a solution of sodium (1 atom) in absolute alcohol with ethyl malonate (1 mol.), and then with phenylthiocarbimide (1 mol.). Instead of collecting the additive product which gradually separates, the mixture, after being kept for several hours, is poured into water, when generally an emulsion is produced from which a solid soon separates. On adding dilute hydrochloric acid to the filtrate from this substance, the ester is precipitated, and when crystallised from alcohol melts at 59—60°, as found by Michael:

0·2044 gave 0·4258 CO_2 and 0·1100 H_2O. C = 56·81; H = 5·97.

$C_{14}H_{17}O_4NS$ requires C = 56·95; H = 5·76 per cent.

The compound referred to above, which is formed along with the thioanilide, crystallises from dilute alcohol in colourless needles; its melting point, 71—72°, and the following analysis characterise it as phenylthiourethane, $C_6H_5·NH·CS·O·C_2H_5$:

0·2095 gave 0·4566 CO_2 and 0·1149 H_2O. C = 59·44; H = 6·09.
0·3030 „ 20 c.c. moist nitrogen at 15° and 754 mm. N = 7·67.
$C_9H_{11}ONS$ requires C = 59·67; H = 6·08; N = 7·62 per cent.

Phenylthiourethane is the only product which is formed on mixing ethyl sodiobenzylmalonate, dissolved in alcohol, with phenyl thiocarbimide; it is precipitated as an oil, which soon solidifies when the alcoholic solution of the mixture is poured into water. The solid was crystallised from alcohol and identified with phenylthiourethane by the melting point and a nitrogen estimation:

0·2415 gave 16·6 c.c. moist nitrogen at 18° and 747 mm. N = 7·79.
$C_9H_{11}ONS$ requires N = 7·62 per cent.

The *diamide*, $C_6H_5·NH·CS·CH(CO·NH_2)_2$. The ester, $C_{14}H_{17}O_4NS$, readily dissolves in ammonia; the solution, which after four days does not deposit a solid, is concentrated in a vacuum at 50°, when a crystalline product separates. This is only sparingly soluble in cold alcohol or water, but readily dissolves in the boiling solvents, and on cooling crystallises in faintly yellow needles which melt and decompose at 176—177°:

0·1985 gave 0·3675 CO_2 and 0·0830 H_2O. C = 50·48; H = 4·64.
0·2010 „ 30·8 c.c. moist nitrogen at 17° and 759 mm. N = 17·75.
$C_{10}H_{11}O_2N_3S$ requires C = 50·63; H = 4·64; N = 17·72 per cent.

The *diamide* is very soluble in ammonia and is reprecipitated by hydrochloric acid.

The *thioanilide* of *malonic acid*, $C_6H_5·NH·CS·CH_2·CO_2H$, is obtained by keeping a solution of the ester, $C_{14}H_{17}O_4NS$, in potassium hydroxide (about 15 per cent.) for three to four days and then adding dilute hydrochloric acid, when it separates in yellow plates; these may be recrystallised from water, in which, on warming, they are moderately soluble, but this operation requires some care, because the substance readily decomposes. The acid, after drying in a vacuum-desiccator over sulphuric acid, melts at 91—92° with evolution of carbon dioxide:

0·2116 gave 0·4292 CO_2 and 0·0890 H_2O. C = 55·31; H = 4·67.
0·2148 „ 13·8 c.c. moist nitrogen at 20° and 750 mm. N = 7·25.
$C_9H_9O_2NS$ requires C = 55·38; H = 4·61; N = 7·18 per cent.

The compound is very soluble in alcohol, and this solution, with ferric chloride, gives a red coloration which disappears on heating. On adding silver nitrate to the ammoniacal or aqueous solutions of the acid, a white precipitate is produced which immediately turns black owing to the formation of silver sulphide.

The thioanilide of malonic acid, when heated on the water-bath until the evolution of carbon dioxide has ceased, yields an oil which on cooling sets to a solid. This crystallises from dilute alcohol in pale yellow prisms; it was identified with thioacetanilide by the melting point 75° and by analysis:

0·2155 gave 17·4 c.c. moist nitrogen at 13° and 746 mm. N = 9·38.
C_8H_9NS requires N = 9·27 per cent.

Diethyl Benzylisothioanilidomethanetricarboxylate, $C_6H_5{\cdot}N{:}C(S{\cdot}CH_2{\cdot}C_6H_5){\cdot}CH(CO_2Et)_2$.

This compound is formed by mixing a solution of sodium (0·5 gram) in absolute alcohol with the thioanilide of diethyl methanetricarboxylate (6·4 grams), dissolved in alcohol, and then adding benzyl chloride (2·7 grams). Sodium chloride begins to separate at the ordinary temperature, and the reaction is complete after an hour's digestion on the water-bath. On distilling off the alcohol, an oil is left behind which, in the course of a day, sets to a solid; this is extremely soluble in alcohol or ether, less so in boiling light petroleum, and, on cooling, crystallises in colourless prisms melting at 64—65°:

0·2098 gave 0·5017 CO_2 and 0·1123 H_2O. C = 65·21; H = 5·94.
0·2672 ,, 8·2 c.c. moist nitrogen at 14° and 768 mm. N = 3·65.
$C_{21}H_{23}O_4NS$ requires C = 65·45; H = 5·92; N = 3·64 per cent.

This compound is insoluble in ammonia or potassium hydroxide; on boiling with dilute hydrochloric acid, it is readily decomposed, and yields aniline and benzyl mercaptan. The latter substance is isolated by distilling the product of the reaction with steam and extracting the distillate with ether. The oil which is left behind on removal of the ether is characterised as a mercaptan by the odour and the formation of a mercury compound; it was identified with benzyl mercaptan by the boiling point, 195°. The presence of aniline in the acid solution was ascertained by the well known tests.

Action of Allylthiocarbimide on Ethyl Sodiomalonate.

This reaction, which is effected in the same way as in the former case, is accompanied by the development of heat. The alcoholic solution of the mixture of reagents, when cold, is poured into water, when an emulsion is produced which is removed by extraction with ether. On adding dilute sulphuric acid to the aqueous layer, a yellow oil is precipitated, which is decomposed even on distillation under diminished pressure. For analysis, the oil was dried in a vacuum desiccator over sulphuric acid; owing to the fact that the substance cannot be purified, the results obtained only approximately agree with those required for the *thioallylamide* of *diethyl methanetricarboxylate*,

$C_3H_5 \cdot NH \cdot CS \cdot CH(CO_2Et)_2$:

0·2099 gave 0·3855 CO_2 and 0·1242 H_2O. C = 50·08; H = 6·57.
$C_{11}H_{17}O_4NS$ requires C = 50·96; H = 6·56 per cent.

The ester readily dissolves in concentrated ammonia, yielding a yellow solution; if this is kept for three days at the ordinary temperature, then concentrated by distillation at about 50° under diminished pressure, and finally treated with dilute hydrochloric acid, the *diamide*, $C_3H_5 \cdot NH \cdot CS \cdot CH(CO \cdot NH_2)_2$, is precipitated. The substance is only sparingly soluble in cold, but readily so in boiling alcohol and, on cooling, crystallises in bunches of colourless needles which melt, not quite sharply, at 184°:

0·2003 gave 0·3067 CO_2 and 0·1035 H_2O. C = 41·76; H = 5·74.
0·1993 „ 35 c.c. moist nitrogen at 13° and 764 mm. N = 20·85.
$C_7H_{11}O_2N_3S$ requires C = 41·79; H = 5·47; N = 20·90 per cent.

Thioanilide of Ethyl Cyanomalonate,
$C_6H_5 \cdot NH \cdot CS \cdot CH(CN) \cdot CO_2Et$.

On adding phenylthiocarbimide to the alcoholic solution of the mixture of sodium ethoxide and ethyl cyanoacetate, heat is developed and colourless crystals of the additive compound separate. The product, when cold, is poured into water, when a white solid is precipitated which is only sparingly soluble in ether or cold alcohol, but dissolves readily in boiling alcohol and, on cooling, crystallises in yellow prisms melting at 118—119°:

0·2128 gave 0·4525 CO_2 and 0·0935 H_2O. C = 57·99; H = 4·88.
0·2305 „ 21·8 c.c. moist nitrogen at 12° and 767 mm. N = 11·33.
$C_{12}H_{12}O_2N_2S$ requires C = 58·06; H = 4·84; N = 11·29 per cent.

The ester, when precipitated from its solutions in alkalis by mineral acids, is colourless and does not turn yellow on drying in a vacuum-desiccator or on dissolving it in cold glacial acetic acid, but a yellow colour is developed on heating the substance in the water-bath or on crystallising it from hot solvents. This behaviour points to the view that the ester exists in two forms; one is colourless and readily changes into the other, which is yellow.

The *thioanilide* of *ethyl cyanomalonate* dissolves in alkalis or, although slowly, in alkali carbonates to form colourless salts.

The *potassium* salt separates from the hot solution of the ester in potassium hydroxide in plates which are sparingly soluble in cold, but readily so in boiling water:

0·3205 gave 0·0970 K_2SO_4. K = 13·57.

$C_{12}H_{11}O_2N_2SK$ requires K = 13·63 per cent.

The *ammonium* salt is isolated by evaporating the solution of the ester in ammonia under diminished pressure. It forms colourless prisms which are moderately soluble in cold, and readily so in boiling water:

0·2118 gave 29·2 c.c. moist nitrogen at 19° and 764 mm. N = 15·92.

$C_{12}H_{15}O_2N_3S$ requires N = 15·85 per cent.

Ethyl benzylisothioanilidocyanomalonate,

$C_6H_5{\cdot}N{:}C(S{\cdot}CH_2{\cdot}C_6H_5){\cdot}CH(CN){\cdot}CO_2Et$,

is formed by mixing the solutions of sodium (0·6 gram) in alcohol with the thioanilide of ethyl cyanomalonate (6·4 grams), dissolved in alcohol, then adding benzyl chloride (3·3 grams) and boiling the mixture on the water-bath for half an hour. On distillation of the alcohol, an oil is left behind which, when cold, sets to a solid. This is washed with water, dried in a vacuum desiccator and dissolved in boiling light petroleum from which, on cooling, it crystallises in colourless prisms melting at 79—80°:

0·2078 gave 0·5128 CO_2 and 0·1004 H_2O. C = 67·30; H = 5·36.

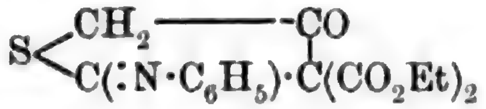
0·2308 ,, 16·4 c.c. moist nitrogen at 17° and 773 mm. N = 8·39.

$C_{19}H_{18}O_2N_2S$ requires C = 67·46; H = 5·33; N = 8·28 per cent.

The substance is very soluble in alcohol or ether; it dissolves sparingly in cold, but readily in boiling light petroleum.

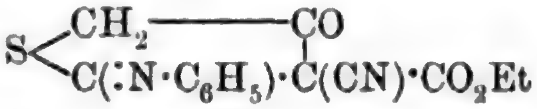
Action of Ethyl Chloroacetate on the Thioanilides of Diethyl Methanetricarboxylate and Ethyl Cyanomalonate.

It has been mentioned before (p. 623) that this reaction yields cyclic compounds which probably have the formulæ:



(I.)

and



(II.)

and accordingly are to be regarded as derivatives of tetrahydrothiophen. The formation of the first (I), *diethyl-2-phenylimino-4-keto-tetrahydrothiophen-3-dicarboxylate*, takes place almost quantitatively on adding to a solution of sodium (0·8 gram) in absolute alcohol, first the thioanilide of diethyl methanetricarboxylate (10·3 grams), dissolved in the same solvent, then ethyl chloroacetate (4·3 grams), and digesting the mixture on the water-bath for an hour. The alcohol is distilled off, and the residue poured into water, when a solid separates. This crystallises from dilute alcohol in yellow prisms which first melt at 115—116°, but immediately solidify again and then only melt again at 135—136°:

0·2042 gave 0·4295 CO_2 and 0·0965 H_2O. C = 57·36 ; H = 5·25.
0·2735 ,, 10 c.c. moist nitrogen at 14° and 752 mm. N = 4·25.
0·2102 ,, 0·1475 $BaSO_4$. S = 9·61.
$C_{16}H_{17}O_5NS$ requires C = 57·31 ; H = 5·07 ; N = 4·18 ; S = 9·56 per cent.

The substance is moderately soluble in cold, readily so in hot alcohol or chloroform. These solutions as well as the crystals are yellow and retain their colour even on boiling the alcoholic solution with animal charcoal.

The compound does not immediately dissolve in potassium hydroxide, but it dissolves on being left in contact with the alkali for some time. After a fortnight, the solution is filtered from the undissolved crystals and treated with hydrochloric acid, when a viscous product is precipitated which, on being kept overnight, sets to a solid. This is dissolved in alcohol, and the solution boiled with animal charcoal; the filtrate, on cooling, yields colourless prisms which soften at 105° and gradually melt at 134°. This substance has the same composition as the yellow compound:

0·2065 gave 0·4344 CO_2 and 0·0947 H_2O. C = 57·37 ; H = 5·09.
0·2263 ,, 8 c.c. moist nitrogen at 15° and 771 mm. N = 4·20.
$C_{16}H_{17}O_5NS$ requires C = 57·31 ; H = 5·07 ; N = 4·18 per cent.

The compound is very stable towards acids and alkalis; when boiled with potassium hydroxide for two hours, it decomposes according to the equation:

$$C_{16}H_{17}O_5NS + 5H_2O = C_6H_5{\cdot}NH_2 + CH_2(CO_2H)_2 + CH_2(SH){\cdot}CO_2H + CO_2 + 2C_2H_6O.$$

The aniline was extracted with ether from the yellow solution, and identified by the usual tests; the alkaline liquor, on treatment with hydrochloric acid, evolved carbon dioxide and, when shaken with ether, gave an oil having the properties of thioglycollic acid; the remaining acid layer was evaporated on the water-bath and the residue extracted with ether; on removal of the ether, colourless crystals were left behind which were recognised as malonic acid by the melting point.

The cyclic compound (II), $C_{14}H_{12}O_3N_2S$, is formed in the same way as its analogue (I). The alcoholic solution of the mixture of sodium ethoxide, the thioanilide of ethyl cyanomalonate and ethyl chloroacetate, when digested on the water-bath, becomes deep red. On distillation of the alcohol, a dark solid is left behind which loses the greater part of the colouring matter by washing with water. The substance is sparingly soluble in cold or boiling alcohol and, after treatment of the solution with animal charcoal, crystallises in yellow prisms which darken at about 205° and melt at 212° to a black liquid:

0·2065 gave 0·4400 CO_2 and 0·0810 H_2O. C = 58·11 ; H = 4·35.
0·2225 „ 19 c.c. moist nitrogen at 18° and 761 mm. N = 9·87.
$C_{14}H_{12}O_3N_2S$ requires C = 58·33 ; H = 4·17 ; N = 9·72 per cent.

This substance resembles the former cyclic compound in its behaviour towards potassium hydroxide, with the difference that it dissolves readily in the warm alkali. On adding dilute hydrochloric acid to this solution, a solid is precipitated which, when crystallised from alcohol with the aid of animal charcoal, is obtained in prisms. These are colourless and, on heating, become discoloured at about 190°, then gradually turn black, and finally melt at 212° to a dark liquid. The identity of this product with the yellow substance was verified by a nitrogen determination:

0·2235 gave 18·4 c.c. moist nitrogen at 14° and 773 mm. N = 9·85.
$C_{14}H_{12}O_3N_2S$ requires N = 9·72 per cent.

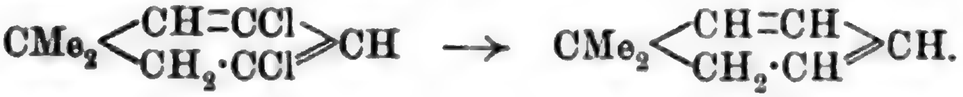
The chief difference which, up to the present, has been found to exist between the two forms, lies in the fact that the one is yellow, the other colourless; besides this I have noticed that the latter compound is more readily soluble in alcohol than the yellow modification. A further study, especially the crystallographic examination, will, most probably, reveal other points of difference.

GONVILLE AND CAIUS COLLEGE,
CAMBRIDGE.

LVIII.—*Substituted Dihydrobenzenes. Part II.* 1 : 1-*Dimethyl-Δ*$^{2:4}$*-dihydrobenzene and* 1 : 1-*Dimethyl-Δ*$^{2:5}$*-dihydrobenzene.*

By ARTHUR WILLIAM CROSSLEY and NORA RENOUF, Salters' Research Fellow.

THE first part of this research contained an account of the preparation of 1 : 1-dimethyl-Δ$^{2:4}$-dihydrobenzene (II) by the reduction of 3 : 5-dichloro-1 : 1-dimethyl-Δ$^{2:4}$-dihydrobenzene (I) with sodium in moist ethereal solution (Trans., 1902, **81**, 821):



$$\mathrm{CMe_2}{<}\begin{matrix}\mathrm{CH{=}CCl}\\ \mathrm{CH_2{\cdot}CCl}\end{matrix}{\geqslant}\mathrm{CH} \longrightarrow \mathrm{CMe_2}{<}\begin{matrix}\mathrm{CH{=}CH}\\ \mathrm{CH_2{\cdot}CH}\end{matrix}{\geqslant}\mathrm{CH}.$$

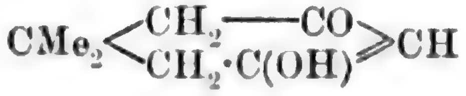
(I.) (II.)

Shortly after the publication of this work, Harries and Antoni (*Annalen*, 1903, **328**, 88) expressed doubt, not only as to the constitution but also as to the composition of this hydrocarbon. Their criticisms were, in part, answered at the time (*Ber.*, 1903, **36**, 2692), but it was considered desirable to try to prepare the substance by another method, in the hope that a comparison of the two specimens of the hydrocarbon would throw further light on the problem. Although many processes have been attempted, it is only recently that one has been successfully carried out, with the result that the correctness of the earlier experiments and deductions are completely confirmed, allowing the following conclusions to be arrived at.

1. The dimethyldihydrobenzene described by Crossley and Le Sueur is 1 : 1-dimethyl-$\Delta^{2:4}$-dihydrobenzene, containing as impurity a very small amount of some oxygenated substance, probably a methoxy-compound.

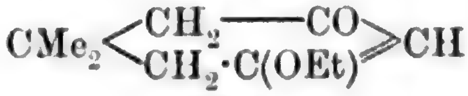
2. The hydrocarbon described in this communication (dimethyldihydrobenzene C and R),* and prepared by the elimination of two molecules of hydrogen bromide from dibromodimethylhexahydrobenzene, is a mixture, in approximately equal quantities, of pure 1 : 1-dimethyl-$\Delta^{2:4}$-dihydrobenzene and pure 1 : 1-dimethyl-$\Delta^{2:5}$-dihydrobenzene.

The starting point in the synthesis was again dimethyldihydroresorcin (III), which was first converted into its ethyl ether (IV) (Trans., 1899, **75**, 775), and this by reduction with sodium in absolute ethyl-alcoholic solution into 3-hydroxy-5-ethoxy-1 : 1-dimethylhexahydrobenzene (V):



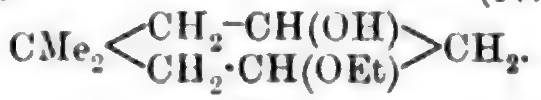
$$\mathrm{CMe_2}<\begin{matrix}\mathrm{CH_2{-}{-}CO}\\ \mathrm{CH_2{\cdot}C(OH)}\end{matrix}\geqslant\mathrm{CH}$$

(III.



$$\mathrm{CMe_2}<\begin{matrix}\mathrm{CH_2{-}{-}CO}\\ \mathrm{CH_2{\cdot}C(OEt)}\end{matrix}\geqslant\mathrm{CH}$$

(IV.)



$$\mathrm{CMe_2}<\begin{matrix}\mathrm{CH_2{-}CH(OH)}\\ \mathrm{CH_2{\cdot}CH(OEt)}\end{matrix}>\mathrm{CH_2}.$$

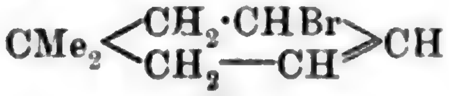
(V.)

This method of preparing the ethoxy-compound is to be preferred to that originally described (Trans., 1907, **91**, 74), on account of the somewhat larger proportion of the compound produced, and also because the various reactions involved are more readily carried out. The yield of ethoxy-compound is 51 per cent. of the theoretical from the ethyl ether used, and there are also produced a resin, containing 1 : 1′-dihydroxy-5 : 5 : 5′ : 5′-tetramethyldi*cyclo*hexane (Trans., 1907, **91**, 71) and a low-boiling liquid, the composition of which is dealt with on page 641.

---

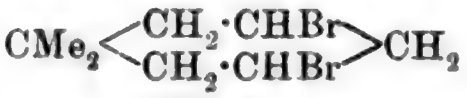
* To avoid confusion as far as possible, the hydrocarbon described in this communication, which is a mixture of pure 1 : 1-dimethyl-$\Delta^{2:4}$-dihydrobenzene and of pure 1 : 1-dimethyl-$\Delta^{2:5}$-dihydrobenzene, is referred to as dimethyldihydrobenzene (C and R), the 1 : 1-dimethyl-$\Delta^{2:4}$-dihydrobenzene, prepared by Crossley and Le Sueur, as dimethyldihydrobenzene (C and S), and the supposed 1 : 1-dimethyl-$\Delta^{2:5}$-dihydrobenzene of Harries and Antoni (*loc. cit.*) as dimethyldihydrobenzene (H and A).

When hydroxyethoxydimethylhexahydrobenzene is treated with fuming hydrobromic acid a mixture of bromodimethyltetrahydrobenzene



$$\mathrm{CMe_2}<\begin{matrix}\mathrm{CH_2\cdot CHBr}\\ \mathrm{CH_2—CH}\end{matrix}>\mathrm{CH}$$

(VI.)

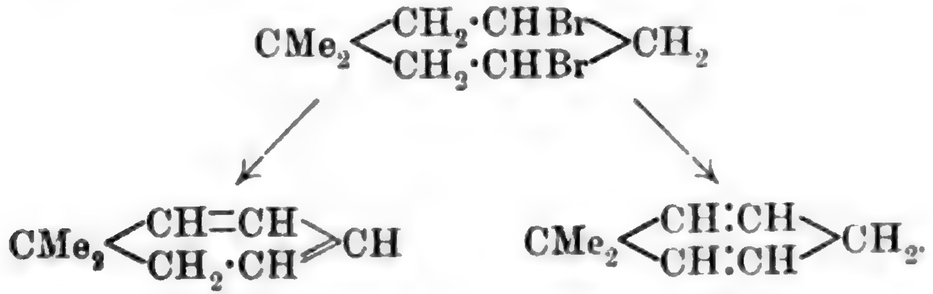


$$\mathrm{CMe_2}<\begin{matrix}\mathrm{CH_2\cdot CHBr}\\ \mathrm{CH_2\cdot CHBr}\end{matrix}>\mathrm{CH_2}$$

(VII.)

(VI) and dibromodimethylhexahydrobenzene (VII) results, in which the latter largely predominates. The presence of the former monobromo-derivative is due to the instability of dibromodimethylhexahydrobenzene and its consequent decomposition with loss of the elements of hydrogen bromide. For this reason, it was impossible to prepare the dibromo-compound in an analytically pure condition, as, no matter how often it was distilled, there was always slight decomposition, resulting in the formation of a small quantity of the lower boiling bromodimethyltetrahydrobenzene. Nor could this latter substance be obtained analytically pure, for it behaves in an exactly similar manner on distillation, giving off the elements of hydrogen bromide with gradual formation of dimethyldihydrobenzene.

When dibromodimethylhexahydrobenzene is treated with quinoline it loses readily and completely two molecules of hydrogen bromide, with formation of dimethyldihydrobenzene, and this reaction may take place in two ways, and two ways only, giving rise to 1 : 1-dimethyl-$\Delta^{2:4}$-dihydrobenzene (VIII), or to 1 : 1-dimethyl-$\Delta^{2:5}$-dihydrobenzene (IX):



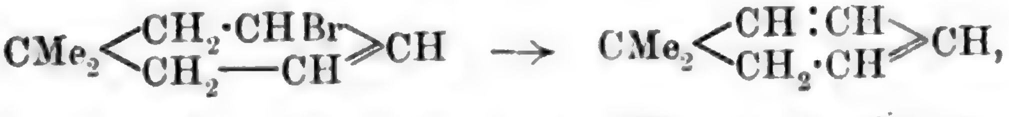
$$\mathrm{CMe_2}<\begin{matrix}\mathrm{CH_2\cdot CHBr}\\ \mathrm{CH_2\cdot CHBr}\end{matrix}>\mathrm{CH_2}$$

$$\swarrow \qquad\qquad \searrow$$

$$\mathrm{CMe_2}<\begin{matrix}\mathrm{CH{=}CH}\\ \mathrm{CH_2\cdot CH}\end{matrix}>\mathrm{CH} \qquad \mathrm{CMe_2}<\begin{matrix}\mathrm{CH{:}CH}\\ \mathrm{CH{:}CH}\end{matrix}>\mathrm{CH_2}.$$

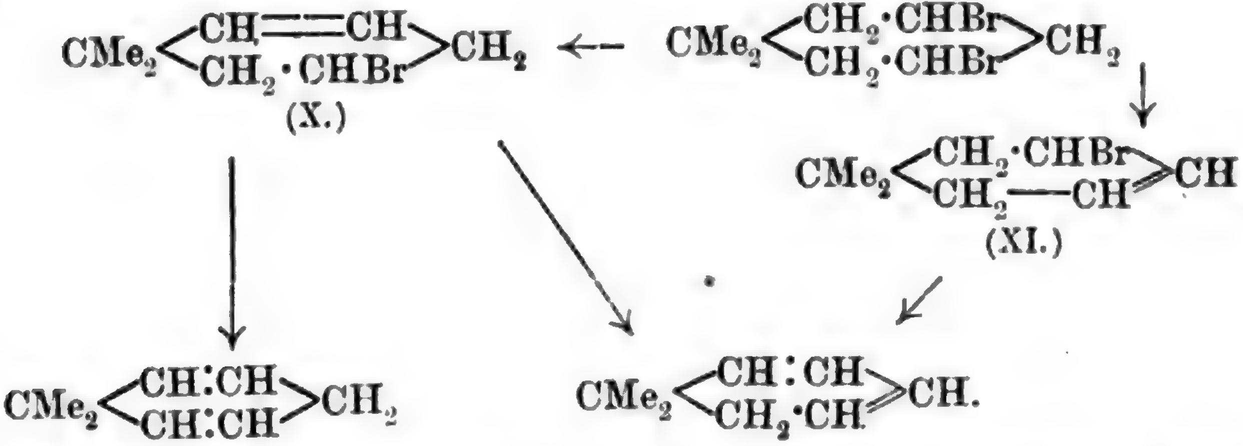
(VIII.) (IX.)

There is no difficulty in proving that the reaction proceeds in both directions, giving rise to a mixture of the two hydrocarbons in approximately equal amounts. At first it was thought that the bromodimethyltetrahydrobenzene might have given only dimethyl-$\Delta^{2:4}$-dihydrobenzene on treatment with quinoline, and the substance was therefore worked up separately,



$$\mathrm{CMe_2}<\begin{matrix}\mathrm{CH_2\cdot CHBr}\\ \mathrm{CH_2—CH}\end{matrix}>\mathrm{CH} \longrightarrow \mathrm{CMe_2}<\begin{matrix}\mathrm{CH{:}CH}\\ \mathrm{CH_2\cdot CH}\end{matrix}>\mathrm{CH},$$

without the slightest indication of any difference in the composition of the resulting hydrocarbon. Nor is this to be surprised at, for if the first product of the action of hydrogen bromide on the ethoxy-compound be dibromodimethylhexahydrobenzene, this may lose hydrogen bromide in two ways to give monobromo-derivatives (X and XI) from which the same mixture of hydrocarbons might result by further loss of hydrogen bromide:



$$\mathrm{CMe_2}<^{\mathrm{CH{=\!=}CH}}_{\mathrm{CH_2\cdot CHBr}}>\mathrm{CH_2} \longleftarrow \mathrm{CMe_2}<^{\mathrm{CH_2\cdot CHBr}}_{\mathrm{CH_2\cdot CHBr}}>\mathrm{CH_2} \longrightarrow \mathrm{CMe_2}<^{\mathrm{CH_2\cdot CHBr}}_{\mathrm{CH_2{-\!-}CH}}>\mathrm{CH}$$

$$\mathrm{CMe_2}<^{\mathrm{CH{:}CH}}_{\mathrm{CH{:}CH}}>\mathrm{CH_2} \qquad \mathrm{CMe_2}<^{\mathrm{CH{:}CH}}_{\mathrm{CH_2\cdot CH}}>\mathrm{CH}.$$

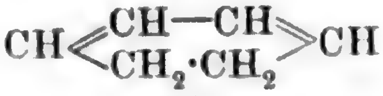
The reasons for believing dimethyldihydrobenzene (C and R) to be a mixture of the two hydrocarbons with the double bonds in the 2 : 4- (formula VIII) and 2 : 5- (formula IX) positions respectively are the following.

1. It contains 1 : 1-dimethyl-$\Delta^{2:4}$-dihydrobenzene because it gives the nitrosochloride of this hydrocarbon (Trans., 1902, **81**, 835).

2. When treated with hydrogen bromide it gives a monohydrobromide and a dihydrobromide. The former boils at 82—83°/20 mm., yields o oxidation *as*-dimethylsuccinic acid, $\beta\beta$-dimethylglutaric acid and the lactone of α-hydroxy-$\beta\beta$-dimethylglutaric acid, and is therefore identical with the hydrobromide of 1 : 1-dimethyl-$\Delta^{2:4}$-dihydrobenzene (Trans., *ibid.*, p. 833), which hydrocarbon, owing to the fact that it contains a conjugated double bond, is only capable of uniting with one molecule of hydrogen bromide, thus corresponding exactly with the behaviour of $\Delta^{1:3}$-dihydrobenzene (Trans., 1904, **85**, 1422) in this respect.

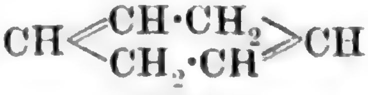
The dihydrobromide is obviously that of 1 : 1-dimethyl-$\Delta^{2:5}$-dihydrobenzene, which, as it contains two double bonds not conjugated, would unite with two molecules of hydrogen bromide.

3. It absorbs bromine to give two distinct bromides, namely, the liquid dibromide of 1 : 1-dimethyl-$\Delta^{2:4}$-dihydrobenzene (Trans., 1902, **81**, 833), and the solid tetrabromide (m. p. 102°) which must be derived from 1 : 1-dimethyl-$\Delta^{2:5}$-dihydrobenzene. Moreover, as the molecular absorption corresponds with three atoms of bromine, it would mean that the mixture consists of the two hydrocarbons in exactly equal amounts. This behaviour is in striking accord with that of dihydrobenzene itself towards bromine, in which case the $\Delta^{1:3}$ variety (XII) absorbs only two atoms to give the solid dibromide (m. p. 108—109°) (Trans., 1904, **85**, 1421), whereas $\Delta^{1:4}$-dihydrobenzene (XIII) adds



$$\mathrm{CH}\lessdot^{\mathrm{CH{-\!-}CH}}_{\mathrm{CH_2\cdot CH_2}}\gtrdot\mathrm{CH}$$

(XII.)

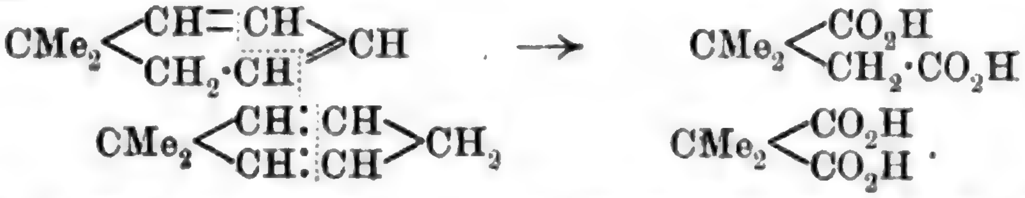


$$\mathrm{CH}\lessdot^{\mathrm{CH\cdot CH_2}}_{\mathrm{CH_2\cdot CH}}\gtrdot\mathrm{CH}$$

(XIII.)

on four atoms of bromine to give a solid tetrabromide melting at 184° (Baeyer, *Annalen*, 1894, **278**, 96).

4. When oxidised with potassium permanganate it yields as main oxidation products *as*-dimethylsuccinic acid and dimethylmalonic acid. The former arises from the 1 : 1-dimethyl-$\Delta^{2:4}$-dihydrobenzene, because, under the conditions used, this hydrocarbon has been shown by experiment not to give rise to any dimethylmalonic acid, which therefore owes its origin to the oxidation of 1 : 1-dimethyl-$\Delta^{2:5}$-dihydrobenzene :



$$\mathrm{CMe_2}\Big<\begin{matrix}\mathrm{CH{=}CH}\\ \mathrm{CH_2{\cdot}CH}\end{matrix}\Big>\mathrm{CH} \longrightarrow \mathrm{CMe_2}\Big<\begin{matrix}\mathrm{CO_2H}\\ \mathrm{CH_2{\cdot}CO_2H}\end{matrix}$$

$$\mathrm{CMe_2}\Big<\begin{matrix}\mathrm{CH{:}CH}\\ \mathrm{CH{:}CH}\end{matrix}\Big>\mathrm{CH_2} \qquad \mathrm{CMe_2}\Big<\begin{matrix}\mathrm{CO_2H}\\ \mathrm{CO_2H}\end{matrix}\,.$$

5. It gives, when treated with a nitrating mixture, the two possible forms of trinitro-*o*-xylene melting at 71° and 115° respectively. This is an exactly analogous reaction to that recorded by Wallach (*Annalen*, 1890, **258**, 329), where 1 : 3-dimethyldihydrobenzene was converted by a mixture of nitric and sulphuric acids into mono-, di-, and trinitro-*m*-xylenes. Now it was not found practicable to prepare a nitro-derivative from 1 : 1-dimethyl-$\Delta^{2:4}$-dihydrobenzene (Trans., 1902, **81**, 833), and the experiments have been repeated with fresh quantities of this hydrocarbon again with the same result. The conclusion to be drawn is obviously that the isomeric 1 : 1-dimethyl-$\Delta^{2:5}$-dihydrobenzene is responsible for the production of the trinitroxylenes in the above-mentioned experiments, during which process a methyl group wanders and, as in other similar cases (Trans., 1904, **85**, 264 ; 1906, **89**, 875), into an ortho-position.

It would appear desirable at this point to give a tabulated comparison of the properties of the dimethyldihydrobenzenes (C and S) and (C and R), also of 1 : 1-dimethyl-$\Delta^{2:4}$-dihydrobenzene and 1 : 1-dimethyl-$\Delta^{2:5}$-dihydrobenzene, as far as can be ascertained from the present experiments (see p. 634).

Having acquired this information, the criticisms of Harries and Antoni (*loc. cit.*) may now be answered in detail.*

In the first place, these authors consider that the analyses given by Crossley and Le Sueur (*ibid.*) are midway between those for a dimethyldihydro- and a dimethyltetrahydro-benzene. The mean of the two analyses quoted gave C = 88·30 and H = 11·27, and it is obvious from the

Difference.	Calculated. C_8H_{14}.	Found.	Calculated. C_8H_{12}.	Difference.
+ 1·03	87·27	C = 88·30	88·88	− 0·58
− 1·46	12·73	H = 11·27	11·11	+ 0·16

annexed comparison that the numbers do not lie midway between

---

* The reply to their remarks about dihydrobenzene has appeared (Trans., 1904, **85**, 1404).

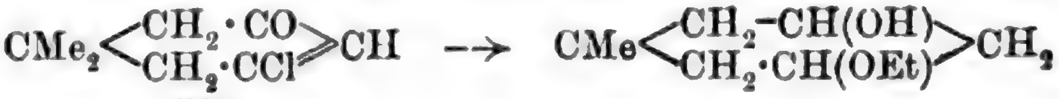
	Dimethyldihydrobenzenes.	
	(C and S).	(C and R).
B. p.	111°	111·2°
Sp. gr. at 15°/15°	0·8153	0·8147
Index of refraction	1·4548	1·4535
Molecular refraction	60·217	60·251
Magnetic rotation	11·024	10·450
Colour with H_2SO_4	Blood-red turning to violet-purple	Blood-red turning to violet-purple
Fuming HBr	Monohydrobromide, b. p. 90·5°/36 mm.	Monohydrobromide, b. p. 83°/20 mm. Dihydrobromide, b. p. 137°/25 mm.
Bromine	Dibromide, unstable liquid	Dibromide, unstable liquid Tetrabromide, m. p. 102°
NOCl	Nitrosochloride, m. p. 121°	Nitrosochloride, m. p. 121°
Nitrating mixture	No definite product	Trinitro-*o*-xylenes, m. p. 71° and 115°
Oxidation products	*as*-Dimethylsuccinic acid	*as*-Dimethylsuccinic acid, dimethylmalonic acid
Oxidation products of monohydrobromide	*as*-Dimethylsuccinic acid, ββ-dimethylglutaric acid, lactone of α-hydroxy-ββ-dimethylglutaric acid	*as*-Dimethylsuccinic acid, ββ-dimethylglutaric acid, lactone of α-hydroxy-ββ-dimethylglutaric acid

1 : 1-Dimethyl-$\Delta^{2:4}$-dihydrobenzene.	1 : 1-Dimethyl-$\Delta^{2:5}$-dihydrobenzene.
Hydrobromide, $C_8H_{13}Br$. B. p. 83°/20 mm.	Hydrobromide, $C_8H_{14}Br_2$. B. p. 137°/25 mm.
Nitrosochloride, m. p. 121°	No nitrosochloride isolated
Dibromide, $C_8H_{12}Br_2$, unstable liquid	Tetrabromide, $C_8H_{12}Br_4$, m. p. 102°
No nitro-derivatives obtainable	Trinitro-*o*-xylenes, m. p. 71° and 115°
Oxidation product, *as*-dimethylsuccinic acid	Oxidation product, dimethylmalonic acid

the calculated figures, the differences in those found and calculated for C_8H_{14} being very large, and the errors are in the wrong direction; for as a rule carbon is found too low and hydrogen too high, and not vice versa. Moreover, if any appreciable quantity of dimethyltetrahydrobenzene had been present it could hardly have escaped detection, as on oxidation it would have yielded ββ-dimethyladipic acid, which presents no difficulty of isolation or identification. This may be noted from the following brief description of some unpublished experiments.

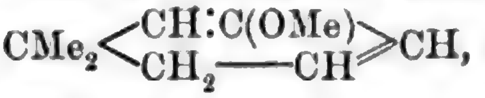
In 1903 an unsuccessful attempt was made to prepare 1 : 1-dimethylhexahydrobenzene (compare Trans., 1905, **87**, 1487) by the reduction of 3 : 5-dichloro-1 : 1-dimethyl-$\Delta^{2:4}$-dihydrobenzene (I) with sodium in amyl-alcoholic solution. The resulting hydrocarbon, after distillation over sodium, boiled at 113—114° and gave the following numbers on analysis, C = 87·96, H = 12·15; that is, midway between those calculated for C_8H_{12} and C_8H_{14}. Further, it gave an orange-brown colour with sulphuric acid, and absorbed two atoms of bromine in chloroform solution (molecular absorption, 156·5). This would be in agreement with the supposition that the hydrocarbon was a mixture of 1 : 1-dimethyl-$\Delta^{2:4}$-dihydrobenzene and 1 : 1-dimethyl-Δ^{3}-tetrahydrobenzene, both of which substances would only absorb two atoms of bromine. On oxidation with potassium permanganate a solid was obtained, which was heated with acetyl chloride, and after evaporation of the solvent the residue was treated with dilute sodium carbonate solution, leaving an insoluble portion, which was proved to consist of *as*-dimethylsuccinic anhydride; after acidification of the sodium carbonate solution with dilute sulphuric acid, ether extracted a white solid crystallising from a mixture of chloroform and light petroleum in stellar aggregates of flattened needles melting at 85—86°, nor was this melting point altered on mixing with pure ββ-dimethyladipic acid. (C = 55·15; H = 8·10. $C_8H_{14}O_4$ requires C = 55·17; H = 8·05 per cent., compare also Trans., 1906, **89**, 1556.)

If the above quoted figures for dimethyldihydrobenzene (C and S) are examined, it will be found that they add up to 99·57; and although this hydrocarbon has been prepared by the old method on fifteen different occasions, and each time analysed, the percentages of carbon and hydrogen found have never together formed 100, the deficit in some cases amounting to as much as 0·8—0·9 per cent. It is therefore acknowledged that the hydrocarbon was not and cannot be obtained in an absolutely pure state by the original method, but the impurity is not dimethyltetrahydrobenzene as suggested by Harries and Antoni. The hydrocarbon was prepared by the action of sodium in moist ethereal solution on dichlorodimethyldihydrobenzene (I), and it might therefore be thought that the impurity was chlorine; but the most stringent tests failed to reveal the slightest trace of this element. Now when chloroketodimethyltetrahydrobenzene (XIV)

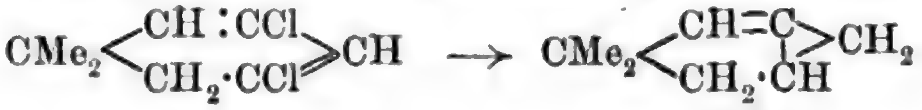


$$CMe_2<\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CCl\end{matrix}>CH \longrightarrow CMe<\begin{matrix}CH_2-CH(OH)\\ CH_2\cdot CH(OEt)\end{matrix}>CH_2$$

(XIV.)

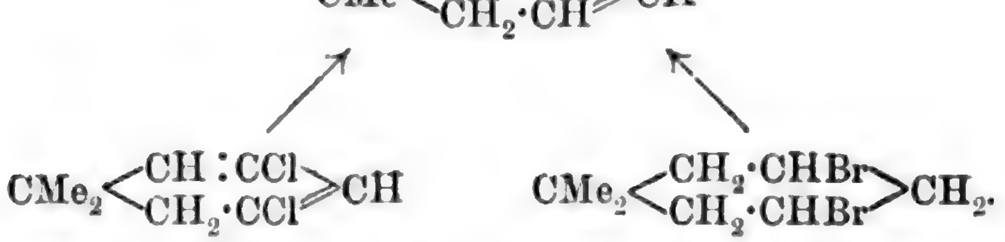
is reduced with sodium in ethyl-alcoholic solution, the chlorine atom is replaced by an ethoxy-group (Trans., 1907, **91**, 74), and it seems most probable that a similar type of reaction takes place in the preparation of 1 : 1-dimethyl-$\Delta^{2:4}$-dihydrobenzene by the reduction of dichlorodimethyldihydrobenzene with sodium in moist ethereal solution; because small quantities of methyl alcohol were added to the ether to facilitate the reaction, and, up to a certain point, the larger the amount of alcohol the more impure was the resulting hydrocarbon. It may therefore be reasonably deduced that the deficit in the above-mentioned analyses is due to oxygen, and that the dimethyldihydrobenzene contains very small amounts of a methoxy-compound, possibly  $CMe_2<\begin{matrix}CH{:}C(OMe)\\ CH_2—CH\end{matrix}>CH$, which would account for the error in the analytical figures.

Another suggestion made by Harries and Antoni is that dimethyldihydrobenzene (C and S) is not a true dihydrobenzene, but contains a trimethylene ring as represented in formula XV. Altogether apart from the probable incapability of existence of such a body, it may be mentioned that the magnetic rotation of the hydrocarbon would have at once proved the presence of a trimethylene ring, and, moreover, we have now evidence that the same dimethyldihydrobenzene is produced by the reduction of dichlorodimethyldihydrobenzene, and by the removal of the elements of hydrogen bromide from dibromodimethylhexahydrobenzene.



$$CMe_2<\begin{matrix}CH{:}CCl\\ CH_2\cdot CCl\end{matrix}>CH \longrightarrow CMe_2<\begin{matrix}CH{=}C\\ |\\ CH_2\cdot CH\end{matrix}>CH_2$$

(XV.)



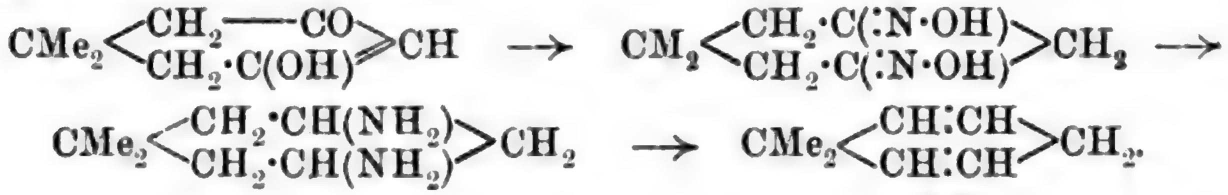
$$CMe<\begin{matrix}CH{:}CH\\ CH_2\cdot CH\end{matrix}>CH$$

$$CMe_2<\begin{matrix}CH{:}CCl\\ CH_2\cdot CCl\end{matrix}>CH \nearrow \qquad \nwarrow CMe_2<\begin{matrix}CH_2\cdot CHBr\\ CH_2\cdot CHBr\end{matrix}>CH_2.$$

This can only be explained if the substance be designated 1 : 1-dimethyl-$\Delta^{2:4}$-dihydrobenzene, and hence the possibility of a trimethylene ring being present in the hydrocarbon is precluded.

Harries and Antoni further point out as a proof that dimethyldihydrobenzene (C and S) is a mixture of the dihydro- and tetrahydro-derivatives, that the physical constants lie midway between those of hydrocarbons of the dihydrobenzene series and those of the tetrahydrobenzene series. The specific gravity, 0·814 at 18°/18°, is, however, not very different from that of 1 : 3-dimethyl-$\Delta^{4:6}$-dihydrobenzene described by Harries, namely, 0·820 at 18°/18°, and, however plausible the above argument may have appeared at the time, it is no longer tenable; for there can be no doubt that dimethyldihydrobenzene (C and R) does not contain any of the corresponding tetrahydro-derivative, yet its physical data do not differ sufficiently from those of dimethyldihydrobenzene (C and S) to bring it in line with those quoted by Harries and Antoni. (See page 634.)

The whole question is further complicated by the fact that Harries and Antoni prepared a hydrocarbon, which they believed to be 1 : 1-dimethyl-$\Delta^{2:5}$-dihydrobenzene, also from dimethyldihydroresorcin as a starting point; but, unfortunately, no information is given as to any derivatives which would enable a comparison to be made with the hydrocarbon having that undoubted structure described in this communication; and it would appear that the present evidence is insufficient definitely to establish the constitution of Harries and Antoni's hydrocarbon. Dimethyldihydroresorcin was first converted into the dioxime, and, after reduction, the dry phosphate of the resulting diamine was distilled:

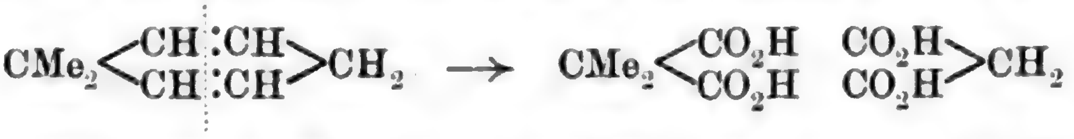


$$\mathrm{CMe_2}\Big\langle\begin{matrix}\mathrm{CH_2{-\!-}CO}\\ \mathrm{CH_2{\cdot}C(OH)}\end{matrix}\Big\rangle\mathrm{CH} \rightarrow \mathrm{CM_2}\Big\langle\begin{matrix}\mathrm{CH_2{\cdot}C(:N{\cdot}OH)}\\ \mathrm{CH_2{\cdot}C(:N{\cdot}OH)}\end{matrix}\Big\rangle\mathrm{CH_2} \rightarrow$$

$$\mathrm{CMe_2}\Big\langle\begin{matrix}\mathrm{CH_2{\cdot}CH(NH_2)}\\ \mathrm{CH_2{\cdot}CH(NH_2)}\end{matrix}\Big\rangle\mathrm{CH_2} \rightarrow \mathrm{CMe_2}\Big\langle\begin{matrix}\mathrm{CH{:}CH}\\ \mathrm{CH{:}CH}\end{matrix}\Big\rangle\mathrm{CH_2}.$$

(XVI.)

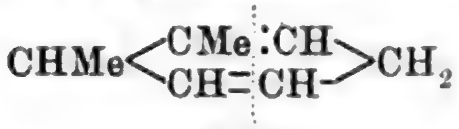
The single piece of evidence on which the supposed constitution of this substance is based is oxidation, whereby 9 grams gave 0·3 gram of oxalic acid, a small amount of a succinic acid, the presence of which could only be proved by the pyrrole reaction, and 2 to 3 grams of an oily acid, consisting for the most part of malonic acid. It is stated that this latter acid could only have been formed if the hydrocarbon has the constitution represented by formula (XVI); in which



$$\mathrm{CMe_2}\Big\langle\begin{matrix}\mathrm{CH{:}CH}\\ \mathrm{CH{:}CH}\end{matrix}\Big\rangle\mathrm{CH_2} \rightarrow \mathrm{CMe_2}\Big\langle\begin{matrix}\mathrm{CO_2H}\\ \mathrm{CO_2H}\end{matrix}\quad\begin{matrix}\mathrm{CO_2H}\\ \mathrm{CO_2H}\end{matrix}\Big\rangle\mathrm{CH_2}$$

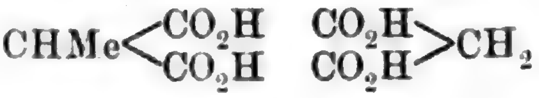
case dimethylmalonic acid should also have been isolated; but Harries and Antoni definitely state that it was impossible to isolate any of this acid. In other words, Harries and Antoni were unable to obtain any oxidation product from the hydrocarbon which contained the *gem*-dimethyl group. Now, although the present authors have oxidised a very large number of derivatives of dimethyldihydroresorcin, they have never failed in any case to isolate either dimethylmalonic acid, *as*-dimethylsuccinic acid, $\beta\beta$-dimethylglutaric acid, the lactone of α-hydroxy-$\beta\beta$-dimethylglutaric acid, or $\alpha\alpha$- or $\beta\beta$-dimethyladipic acids, that is, an oxidation product definitely proving the presence of the *gem*-dimethyl group.

It is possible that during the distillation of the diamine phosphate a methyl group has wandered, whence Harries and Antoni's hydrocarbon might have the constitution represented by formula (XVII),



$$\mathrm{CHMe}<\begin{matrix}\mathrm{CMe{:}CH}\\ \mathrm{CH{=}CH}\end{matrix}>\mathrm{CH_2}$$

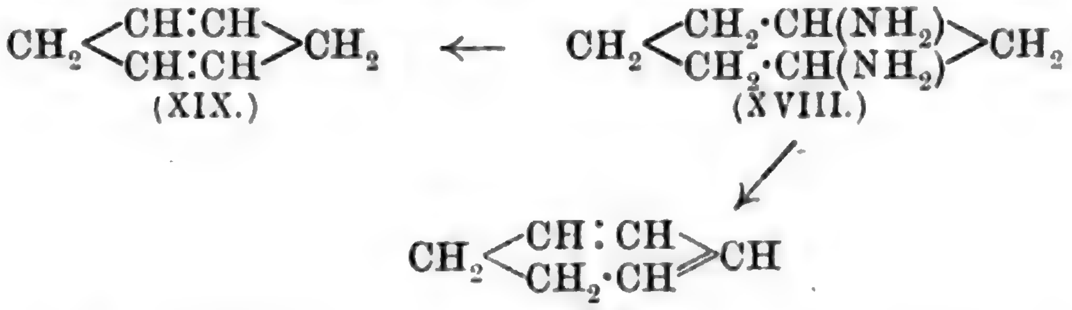
(XVII.)



$$\mathrm{CHMe}<\begin{matrix}\mathrm{CO_2H} & \mathrm{CO_2H}\\ \mathrm{CO_2H} & \mathrm{CO_2H}\end{matrix}>\mathrm{CH_2}$$

and from which malonic acid could easily result on oxidation.

Nor is there any apparent reason, presuming that a methyl group does not wander, for supposing that the elimination of ammonia from the cyclic diamine would take place in one way and one way only. Harries and Antoni have themselves shown that, when the phosphate of diaminohexahydrobenzene (XVIII) is submitted to dry distillation, ammonia is evolved in both of the possible directions, giving rise to a mixture of $\Delta^{1:3}$-dihydrobenzene (XX) and $\Delta^{1:4}$-dihydrobenzene (XIX),



$$\mathrm{CH_2}<\begin{matrix}\mathrm{CH{:}CH}\\ \mathrm{CH{:}CH}\end{matrix}>\mathrm{CH_2} \leftarrow \mathrm{CH_2}<\begin{matrix}\mathrm{CH_2{\cdot}CH(NH_2)}\\ \mathrm{CH_2{\cdot}CH(NH_2)}\end{matrix}>\mathrm{CH_2}$$

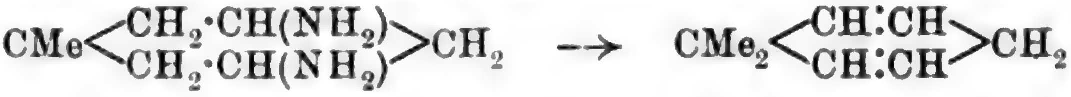
(XIX.) (XVIII.)

$$\swarrow$$

$$\mathrm{CH_2}<\begin{matrix}\mathrm{CH{:}CH}\\ \mathrm{CH_2{\cdot}CH}\end{matrix}>\mathrm{CH}$$

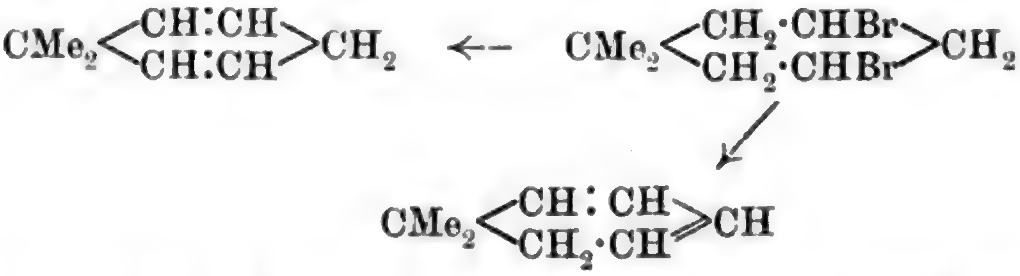
(XX.)

and they therefore conclude that "the *gem*-dimethyl group influences the position taken up by the double bonds,"



$$\mathrm{CMe}<\begin{matrix}\mathrm{CH_2{\cdot}CH(NH_2)}\\ \mathrm{CH_2{\cdot}CH(NH_2)}\end{matrix}>\mathrm{CH_2} \longrightarrow \mathrm{CMe_2}<\begin{matrix}\mathrm{CH{:}CH}\\ \mathrm{CH{:}CH}\end{matrix}>\mathrm{CH_2}$$

If this is so, why does it not influence the position of the double bonds when hydrogen bromide is eliminated from dibromodimethylhexahydrobenzene? For this is a reaction strictly analogous to the above, which, as proved in this communication, takes place in both ways, giving rise to a mixture of the two possible hydrocarbons in equal amounts. The presence of the *gem*-dimethyl group certainly does not exercise any apparent influence in this case, or in the position of the double bond formed when 3-bromo-1 : 1-dimethylhexa-

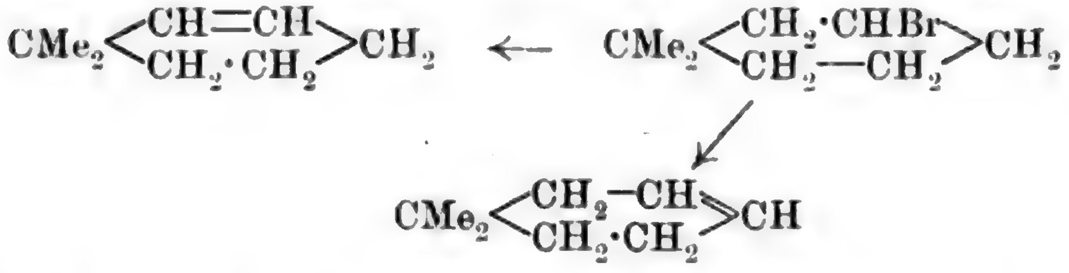


$$\mathrm{CMe_2}<\begin{matrix}\mathrm{CH{:}CH}\\ \mathrm{CH{:}CH}\end{matrix}>\mathrm{CH_2} \leftarrow \mathrm{CMe_2}<\begin{matrix}\mathrm{CH_2{\cdot}CHBr}\\ \mathrm{CH_2{\cdot}CHBr}\end{matrix}>\mathrm{CH_2}$$

$$\swarrow$$

$$\mathrm{CMe_2}<\begin{matrix}\mathrm{CH{:}CH}\\ \mathrm{CH_2{\cdot}CH}\end{matrix}>\mathrm{CH}$$

hydrobenzene loses the elements of hydrogen bromide (Trans., 1906, **89**, 1556), when again two isomeric hydrocarbons are produced.



$$\mathrm{CMe_2}\left<\begin{matrix}\mathrm{CH{=}CH}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}\right>\mathrm{CH_2} \quad\longleftarrow\quad \mathrm{CMe_2}\left<\begin{matrix}\mathrm{CH_2\cdot CHBr}\\ \mathrm{CH_2{-}CH_2}\end{matrix}\right>\mathrm{CH_2}$$

$$\swarrow$$

$$\mathrm{CMe_2}\left<\begin{matrix}\mathrm{CH_2{-}CH}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}\right>\mathrm{CH}$$

The boiling point of dimethyldihydrobenzene (H and A) is 135—137°, agreeing very well with the boiling points of other dimethyldihydrobenzenes, whereas dimethyldihydrobenzene (C and S) boils at 111°, and Harries and Antoni suggest that the low boiling point may be due to the fact that it is a mixture of dimethyldi- and dimethyltetra-hydrobenzenes, but again this argument is not tenable, for dimethyldihydrobenzene (C and R) boils at precisely the same temperature. It is true that this latter hydrocarbon is a mixture of dimethyl-$\Delta^{2:4}$-dihydrobenzene and dimethyl-$\Delta^{2:5}$-dihydrobenzene, and we have no information as to the lowering of the boiling point in a mixture of two substances differing in constitution only by the varying positions of the double bonds. It seems hardly likely, however, that this would lower the boiling point by 26°, and it would, indeed, be a most remarkable coincidence if the minute amount of impurity in dimethyldihydrobenzene (C and S) should cause exactly the same lowering in the boiling point of dimethyl-$\Delta^{2:4}$-dihydrobenzene as would be observed by mixing a pure specimen of this hydrocarbon with an equal bulk of pure dimethyl-$\Delta^{2:5}$-dihydrobenzene, yet such is the composition of the dimethyldihydrobenzene (C and R). It is hoped that before long further information will be forthcoming as to what influence, if any, the presence of certain groupings exercises on the boiling point of isomeric substituted dihydrobenzenes.

Harries and Antoni state that 2 grams of their dimethyldihydrobenzene gave, on treatment with a nitrating mixture, 0·6 gram of trinitro-*m*-xylene, but they do not give the melting point of the product, and consequently it is doubtful which of the three trinitro-*m*-xylenes (melting respectively at 90°, 125°, and 182°) was obtained. But this might be regarded as a proof that dimethyldihydrobenzene (H and A) does not contain the *gem*-dimethyl group, for although many cases of the wandering of a methyl group in derivatives of *gem*-dimethyldihydroresorcin have been recorded (Trans., 1904, **85**, 264; 1906, **89**, 875), no single instance has been observed in which a methyl group has wandered into anything but an ortho-position. Moreover, dimethyldihydrobenzene (C and R) undoubtedly contains dimethyl-$\Delta^{2:5}$-dihydrobenzene, and under the influence of a nitrating mixture it is this hydrocarbon which is converted into the two possible trinitro-*o*-xylenes, as explained on page 633.

With the statement of Harries and Antoni that dimethyldihydrobenzene (C and S) also gives trinitro-*m*-xylene we cannot agree, as all attempts to nitrate this hydrocarbon under the conditions mentioned by Harries and Antoni, and also under various other conditions, have failed to give any definite nitro-derivative.

EXPERIMENTAL.

Preparation of 1 : 1-*Dimethyldihydroresorcin Ethyl Ether.*

The ethyl ether of dimethyldihydroresorcin was originally prepared (Trans., 1899, **75**, 775) by the action of ethyl iodide on the silver salt of dimethyldihydroresorcin, but it may be more readily obtained in bulk by direct esterification. For this purpose, large amounts of dimethyldihydroresorcin were heated in quantities of 50 grams with 150 grams of absolute ethyl alcohol and 15 grams of concentrated sulphuric acid for seven hours in a flask attached to a reverse condenser. The major quantity of the alcohol was then evaporated, the residue poured into water, extracted three times with ether, the ethereal solution washed with potassium hydroxide solution (washings = A), then water, dried over calcium chloride, and the ether evaporated, when the residue of 38—40 grams set at once to a solid cake, which, after one crystallisation from light petroleum (b. p. 40—60°), melted sharply at 60°.

On acidifying the alkaline washings, A, 16 grams of dimethyldihydroresorcin were recovered, which were again esterified in the above-described manner, when the total yield of ethyl ether was brought up to 78 per cent. of the theoretical.

Reduction of the Ether with Sodium and Absolute Alcohol.

Four hundred and fifty grams of the ether were dissolved in quantities of 20 grams (1 molecule) at one time in 400 c.c. of absolute ethyl alcohol in a flask attached to a reverse condenser, and 33 grams of sodium (12 atoms) cut in thin slices gradually added; the flask was continuously shaken and heated to expedite the solution of the last portions of the sodium. Water was then added, and sufficient alcohol evaporated to cause the separation of an oil, when the whole was extracted four times with ether, washed with water until no longer alkaline, dried over calcium chloride and, after evaporation of the ether, distilled, when at 33 mm. the following fractions were collected:

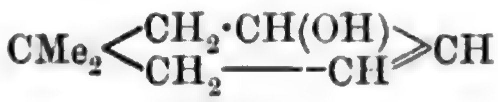
Below 130° = 61 grams; 130—145° = 225 grams; resinous residue = 31 grams, and after two more distillations:

87—120° = 45 grams; 120—135° = 2 grams; 135—138° = 236 grams.

Fraction 87—120°.—The boiling point of this material, which is identical in composition with the similar low boiling liquid obtained by the reduction of chloroketodimethyltetrahydrobenzene with sodium in alcoholic solution (Trans., 1907, **91**, 74), showed it to be a mixture, but after repeated fractionation a small portion boiled constantly at 85° at 23 mm., and gave the following numbers on analysis:

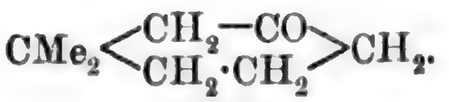
0·1424 gave 0·3985 CO_2 and 0·1373 H_2O. C = 76·32; H = 10·71.
$C_8H_{14}O$ requires C = 76·19; H = 11·11 per cent.

It was expected that this substance would prove to be 3-keto-1 : 1-dimethyl-Δ^4-tetrahydrobenzene, $C_8H_{12}O$ (Trans., 1907, **91**, 78), but the analysis shows it to contain at most traces of this ketone and to have the formula $C_8H_{14}O$. It must therefore be either 3-hydroxy-1 : 1-dimethyl-Δ^4-tetrahydrobenzene (XXI), or 3-keto-1 : 1-dimethylhexahydrobenzene (XXII):



$$\mathrm{CMe_2}<\begin{matrix}\mathrm{CH_2\cdot CH(OH)}\\ \mathrm{CH_2\text{———}CH}\end{matrix}>\mathrm{CH}$$

(XXI.)



$$\mathrm{CMe_2}<\begin{matrix}\mathrm{CH_2{-}CO}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{CH_2}.$$

(XXII.)

Inasmuch as it did not give a semicarbazone but gave acetyl and benzoyl derivatives, and also as its boiling point is 10° higher than that of keto-1 : 1-dimethylhexahydrobenzene (Trans., 1907, **91**, 81), it would appear to be 3-*hydroxy*-1 : 1-*dimethyl*-Δ^4-*tetrahydrobenzene.*

It is a clear, colourless, limpid liquid, with a strong camphoraceous odour, giving only a faint orange colour with sulphuric acid, and absorbing bromine in chloroform solution without evolving hydrogen bromide. It did not solidify when cooled in a freezing mixture. Unfortunately, the acetyl and benzoyl derivatives could not be obtained in an analytically pure condition, as there was too little of the fraction boiling at 85° at 23 mm. In order to prove the presence of 3-keto-1 : 1-dimethyl-Δ^4-tetrahydrobenzene, the fraction 84—86°, giving a marked colour reaction with sulphuric acid, was treated with benzoyl chloride, and, after working up in the usual way, distilled at 25 mm., when about one-third of the liquid passed over below 100°, and the temperature then rose rapidly to 190° (boiling point of the benzoyl derivative). The low boiling liquid was reduced with zinc dust in aqueous alcoholic solution, when a quantity of 1 : 1′-dihydroxy-5 : 5 : 5′ : 5′-tetramethyl-$\Delta^{2:2'}$-di*cyclo*hexene, melting at 148°, was obtained, and from this, by treatment with bromine, the tribromo-anhydride (?) melting with decomposition at 250° (Trans., 1907, **91**, 76).

The fraction 87—120° therefore consisted of 3-keto-1 : 1-dimethyl-Δ^4-tetrahydrobenzene, 3-hydroxy-1 : 1-dimethyl-Δ^4-tetrahydrobenzene, and probably also the corresponding saturated ketone and alcohol, the production of which substances necessitates the elimination of the elements of ethyl alcohol from the ethoxy-compound during the process of reduction. If the fraction contained nothing but these substances, then on reduction the whole should be converted into the fully saturated alcohol, and by treating 30 grams with sodium in moist ethereal solution (Trans., 1905, **87**, 1494), there were produced 22 grams of 3-hydroxy-1 : 1-dimethylhexahydrobenzene and 3·5 grams of a resin yielding 1·5 grams of 1 : 1′-dihydroxy-5 : 5 : 5′ : 5′-tetramethyl-di*cyclo*hexane, melting at 212° (Trans., 1907, **91**, 71). The latter substance was also obtained by working up the 31 grams of resinous residue mentioned above.

The fraction 135—138° was again distilled, when the major portion boiled constantly at 131° at 25 mm.:

0·1229 gave 0·3158 CO_2 and 0·1288 H_2O. C = 70·07 ; H = 11·64.

$C_{10}H_{20}O_2$ requires C = 69·77 ; H = 11·62 per cent.

3-Hydroxy-5-ethoxy-1 : 1-dimethylhexahydrobenzene, which is obtained in 51 per cent. of the theoretical quantity from the ethyl ether used, possesses the properties already ascribed to it (Trans., 1907, **91**, 74).

Action of Hydrogen Bromide on Hydroxyethoxydimethylhexahydrobenzene.

Two hundred and fifty grams of hydroxyethoxydimethylhexahydrobenzene were treated with fuming hydrobromic acid exactly as previously described (Trans., 1905, **87**, 1497), except that the heating was carried out in glass stoppered bottles instead of soda-water bottles. After several distillations of the product, the following fractions were obtained:

80—90° = 1 gram; 90—100° = 9·0 grams; 100—110° = 24 grams; 110—120° = 11·0 grams; 120—130° = 5·5 grams; 130—150° = 216 grams.

The residue of 44 grams was not further worked with.

The fraction 100—110° was twice redistilled, and a portion boiling at 92—93° at 40 mm. analysed:

0·1431 gave 0·2852 CO_2 and 0·1011 H_2O. C = 54·35 ; H = 7·85.

0·1866 „ 0·1635 AgBr. Br = 37·28.

$C_8H_{13}Br$ requires C = 50·79 ; H = 6·87 ; Br = 42·33 per cent.

As the analytical numbers add up to 99·5, there can be no doubt that the substance contained only carbon, hydrogen and bromine, and consisted mainly of bromodimethyltetrahydrobenzene, mixed probably with some dimethyldihydrobenzene; for on distillation there was always slight decomposition due to loss of hydrogen bromide and formation of small quantities of a lower boiling substance.

The fraction 130—150° was redistilled, when practically the whole boiled between 135—138° at 25 mm.:

0·1599 gave 0·2208 CO_2 and 0·0777 H_2O. C = 37·66; H = 5·39.
0·1318 „ 0·1756 AgBr. Br = 56·69.
$C_8H_{14}Br_2$ requires C = 35·55; H = 5·18; Br = 59·25 per cent.

The analytical figures add up to 99·74, showing the absence of oxygen, and this material evidently consisted of a mixture of bromodimethyltetrahydrobenzene and dibromodimethylhexahydrobenzene, as the context shows. Further distillation only resulted in the evolution of hydrogen bromide and production of the monobromide of lower boiling point.

Treatment of the Mixed Bromides with Quinoline.

Having proved that the low and high boiling bromides gave the same substance under the influence of quinoline, the whole of the material was treated in the following manner. Forty grams of the bromide and 80 grams of freshly-distilled quinoline were heated in a distillation flask, the neck of which was eight inches long. A reaction set in at 167°, and proceeded quietly at 175°, the hydrocarbon distilling over. Finally, the thermometer was raised out of the liquid, and everything allowed to distil which would do so below a temperature of 200°. As one such treatment did not give a product free from halogen, the distillate was again heated with its own weight of quinoline in the long-necked flask for one and a-half hours at a temperature just sufficiently high to keep the liquid boiling, but not to allow any hydrocarbon to pass over. The temperature was then raised, the hydrocarbon collected, and steam distilled from dilute sulphuric acid to remove quinoline. The product contained the merest trace of bromine, which was entirely removed by distillation in air, when the small residue boiling above 150° was found to contain the bromine. The hydrocarbon (73 grams from 249 grams of bromide) was then fractionated over metallic sodium, using a Young's rod and disk still-head (15 disks):

	1st Fractionation. Grams.	2nd Fractionation. Grams.
111—113°	1	1
113—115°	43·5	50·8
115—120°	16·0	9·5
Residue	9·5	6·0

The portion 113—115° was twice refractionated, when practically the whole distilled between 111° and 112°:

0·1425 gave 0·4635 CO_2 and 0·1462 H_2O. C = 88·71 ; H = 11·39.
C_8H_{12} requires C = 88·88 ; H = 11·11 per cent.

Dimethyldihydrobenzene (C and R) is a clear, colourless, highly refractive liquid, boiling at 111·2° at 749 mm., and possessing a faint odour of garlic, yet strongly resembling turpentine. When dissolved in alcohol and treated with concentrated sulphuric acid, it gives a blood-red colour, rapidly turning to deep plum colour, and then slowly changing to deep violet purple. As proved by the context, it is a mixture of 1 : 1-dimethyl-$\Delta^{2:4}$-dihydrobenzene and 1 : 1-dimethyl-$\Delta^{2:5}$-dihydrobenzene in almost equal amounts.

The boiling point of the fractions of the hydrocarbon distilling above 112° was found to be lowered by each further distillation, but the higher fractions were too small to investigate completely. Two of these were analysed and their bromine absorptions determined:

	Carbon.		Hydrogen.		
	Found.	Calc.	Found.	Calc.	Bromine absorption.
Fraction 118—121°	88·69	88·88	11·23	11·11	156·8
„ 125—130	88·44	88·88	11·48	11·11	156·5

This proves that the whole material had the composition of a dimethyldihydrobenzene, and the presence of the small quantity of this higher boiling substance may be due to polymerisation.

The bromine absorptions were done before it had been noticed that a further amount of bromine is very slowly absorbed by the hydrocarbon (see page 650), and, on repeating the determination with a portion of the hydrocarbon boiling at 120—130°, the first end-point showed a molecular absorption of 159 and the second end-point 235. On evaporating the chloroform mother liquor, the tetrabromide melting at 102° was obtained (see p. 650). The following physical data, kindly sent to us by Dr. F. M. Perkin, refer to the hydrocarbon boiling at 111·2°, and were determined by the late Sir W. H. Perkin.

Density determinations:

d 4°/4° = 0·82374 ; d 15°/15° = 0·81470 ; d 25°/25° = 0·80737.

Magnetic rotation:

t.	Sp. rot.	Mol. rot.
15·7	1·4977	10·4505

Refractive value :
d 16·3°/4° = 0·81291.

Line.	t.	Index of refraction μ.	Specific refraction $\frac{\mu-1}{d}$	Molecular refraction $\frac{\mu-1}{d}p$.	Calculated.
H_α	16·3	1·453513	0·55788	60·251	60·2
H_β	16·3	1·465146	0·57219	61·796	
H_γ	16·3	1·472501	0·58124	62·777	

Dispersion $H_\gamma - H_\alpha$ 2·526.

The first specimen of dimethyldihydrobenzene (C and S) examined was in 1902 (Trans., **81**, 836), but, although the numbers were considered to prove definitely that the substance was a dimethyldihydrobenzene, the subsequent comparison of these numbers with the values obtained in the case of dimethyltetrahydrobenzene and dimethylhexahydrobenzene led Sir W. H. Perkin to express the opinion that the dimethyldihydrobenzene contained a small amount of some impurity, which is now admitted (see page 636). It will be noticed that the numbers for pure dimethyldihydrobenzene (C and R) given above do actually differ from those for dimethyldihydrobenzene (C and S) as seen in the following table :

	Density 15°/15°.	Mol. rot.	Mol. refraction $\frac{\mu-1}{d}p$.
C and S	0·8153	11·0240	60·217
C and R	0·8147	10·4505	60·251

As regards the magnetic rotation, this determination completes the investigation of a series of compounds commencing with dimethylhexahydrobenzene and ending with *o*-xylene, and the changes in physical properties following the loss of two, four, or six hydrogen atoms can be followed.

	Mol. rot.	Difference.
Dimethylhexahydrobenzene (Trans., 1905, **87**, 1491)......	8·150	
		0·753
Dimethyltetrahydrobenzene (*ibid.*)...............................	8·903	
		1·547
Dimethyldihydrobenzene (see above)...........................	10·450	
		2·895
o-Xylene (Trans., 1896, **69**, 1241)	13·345	

These numbers may be compared with another completed set, namely, hexahydrobenzene to benzene :

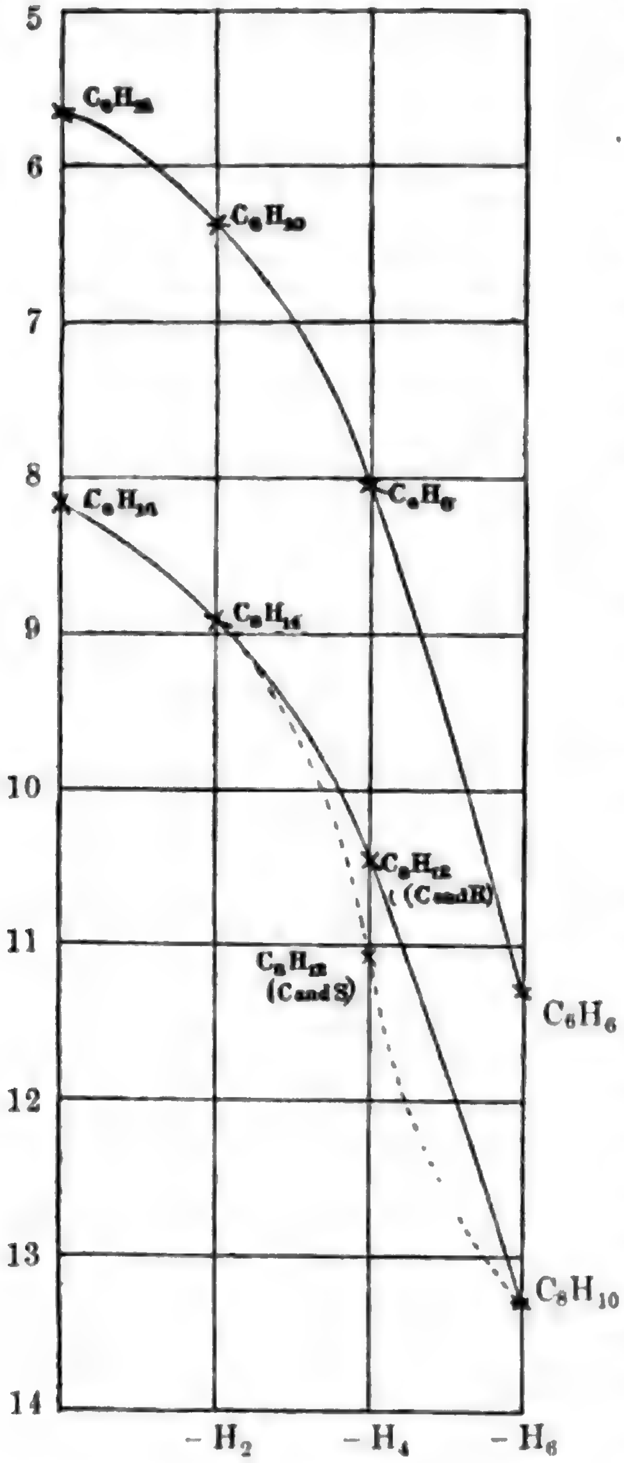
	Mol. rot.	Difference.
Hexahydrobenzene (Trans., 1900, **77**, 372)	5·664	
		0·731
Tetrahydrobenzene (Trans., 1898, **73**, 942)	6·395	
		1·698
Dihydrobenzene (Trans., 1904, **85**, 1417).	8·093	
		3·191
Benzene (Trans., 1896, **69**, 1241)	11·284	

by Google

It is very interesting to note that when these figures are plotted out they form almost regular curves practically identical in form.

The dotted line shows the course of the curve if the number for dimethyldihydrobenzene (C and S) is included, in which case the form of the curve differs decidedly from that obtained for hexahydrobenzene to benzene.

FIG. 1.



Action of Nitric Acid.—Three grams of the hydrocarbon were added drop by drop to a mixture of 23 c.c. of fuming nitric acid and 11 c.c. of concentrated sulphuric acid, cooled in ice, and allowed to stand twenty-four hours, when an oil had separated. It is important that the addition of the hydrocarbon to the nitrating mixture should be made very gradually, otherwise oxidation takes place very violently with production of flame. The whole was then heated on the water-bath for one hour, poured into water, and the separated oil heated on the water-bath for twelve hours with 30 c.c. of a mixture of one volume of fuming nitric acid and two volumes of concentrated sulphuric acid. On standing twelve hours, compact, needle-shaped crystals had separated, these were filtered off (filtrate = A), washed with water, dried on a porous plate, and purified by crystallisation from ethyl alcohol:

0·1007 gave 15·1 c.c. moist nitrogen at 17° and 752 mm. N = 17·21.
$C_8H_7O_6N_3$ requires N = 17·43 per cent.

This nitro-compound crystallised from ethyl alcohol in white, glistening needles melting at 115°, nor was this melting point altered on mixing with pure trinitro-*o*-xylene melting at 115° (Proc., 1908, **24**, 58), with which substance it is identical. The amount obtained was 0·4 gram.

The filtrate A (see above) was poured into water and allowed to stand, when one gram of a solid separated. It was purified by crystallisation from alcohol and the nitrogen determined :

0·1439 gave 21·8 c.c. moist nitrogen at 17° and 748 mm. N = 17·30.
$C_8H_7O_6N_3$ requires N = 17·43 per cent.

This substance crystallises from absolute alcohol in small, faintly yellow, flattened needles melting at 71°, and is identical with the trinitro-*o*-xylene melting at 71° (Proc., *loc. cit.*).

The nitration was then repeated under the conditions described by Harries and Antoni (*ibid.*, p. 111), when 2 grams of the hydrocarbon gave 0·6 gram of solid which consisted of a mixture of the two trinitro-*o*-xylenes melting respectively at 71° and 115°.

On finding that dimethyldihydrobenzene (C and R) readily gave these nitro-derivatives, whereas it had not been found possible to nitrate dimethyldihydrobenzene (C and S), the latter was again prepared and treated exactly as described above. After heating one hour and pouring into water, 2 grams of the hydrocarbon gave 2·5 grams of a yellow semi-solid, which could not be brought into a crystalline condition, and decomposed with evolution of nitrous fumes without previously melting. After treatment with the second nitrating mixture, only 0·2 gram of a similar yellow material was obtained, from which no definite chemical individual could be isolated.

The nitration of dimethyldihydrobenzene (C and S) was then attempted, using the conditions employed by Harries and Antoni, but not a trace of trinitro-*m*-xylene or any other crystalline substance could be obtained.

A *nitroso-chloride* was prepared as previously described (Trans., 1902, **81**, 835), and also by passing nitrosyl chloride into a dry chloroform solution of the hydrocarbon kept below −10° and then pouring into four times the volume of methyl alcohol. By the first method, 4 grams of the hydrocarbon gave 0·1 gram, and by the second method 0·2 gram of a solid crystallising from methyl alcohol in fine, white, silky needles, melting at 121°. As the melting point is also a decomposition point, it varies according to conditions. On heating as rapidly as possible to 100° and then using a very small flame, the above temperature was noted, nor was this melting point altered on admixture with an equal bulk of the nitroso-chloride prepared from dimethyldihydrobenzene (C and S) (Trans., 1902, **81**, 835). It is interesting to note the yield of this nitroso-chloride, namely, 0·2 gram from 4 grams of dimethyldihydrobenzene (C and R).

This latter hydrocarbon contains approximately 50 per cent. of 1 : 1-dimethyl-$\Delta^{2:4}$-dihydrobenzene and 1 : 1-dimethyl-$\Delta^{2:5}$-dihydrobenzene, and therefore in reality 2 grams of dimethyldihydrobenzene (C and R) give 0·2 gram of the nitroso-chloride, or exactly the same yield as when prepared from dimethyldihydrobenzene (C and S) namely, 0·5 gram from 5 grams of the hydrocarbon.

Although very careful search was made, no evidence could be obtained of the production of a nitroso-chloride from the isomeric 1 : 1-dimethyl-$\Delta^{2:5}$-dihydrobenzene.

Action of Fuming Hydrobromic Acid.—Fifteen grams of the hydrocarbon were treated with hydrobromic acid exactly as previously described (Trans., 1902, **81**, 833). The residue was distilled at 22 mm., when 15·5 grams were obtained boiling at 90—130°, and 13·5 grams at 130—132°. After repeated fractionation of the portion boiling at 90—130°, 10 grams passed over constantly at 82—83° at 20 mm., and gave on analysis a number for bromine agreeing with the addition of one molecule of hydrogen bromide to the hydrocarbon. This boiling point is the same as that of the hydrobromide of dimethyldihydrobenzene (C and S) (Trans., 1902, **81**, 833), namely, 90·5° at 36 mm. (not 16 mm. as stated), and identity was further proved by oxidation, when there were produced *as*-dimethylsuccinic acid, small quantities of ββ-dimethylglutaric acid, and the lactone of α-hydroxy-ββ-dimethylglutaric acid. The process of oxidation was that previously described (Trans., 1903, **83**, 118).

In order to make certain that the hydrobromide boiling at 82—83° at 20 mm. would not combine with more hydrogen bromide, it was again treated with fuming hydrobromic acid and allowed to stand forty-eight hours. The boiling point of the resulting liquid was unchanged, and a bromine determination gave the same value as after the first treatment with hydrobromic acid.

The fraction 130—132° on redistillation boiled quite constantly at 137° at 25 mm.:

0·1869 gave 0·2628 AgBr. Br = 59·83.

$C_8H_{14}Br_2$ requires Br = 59·26 per cent.

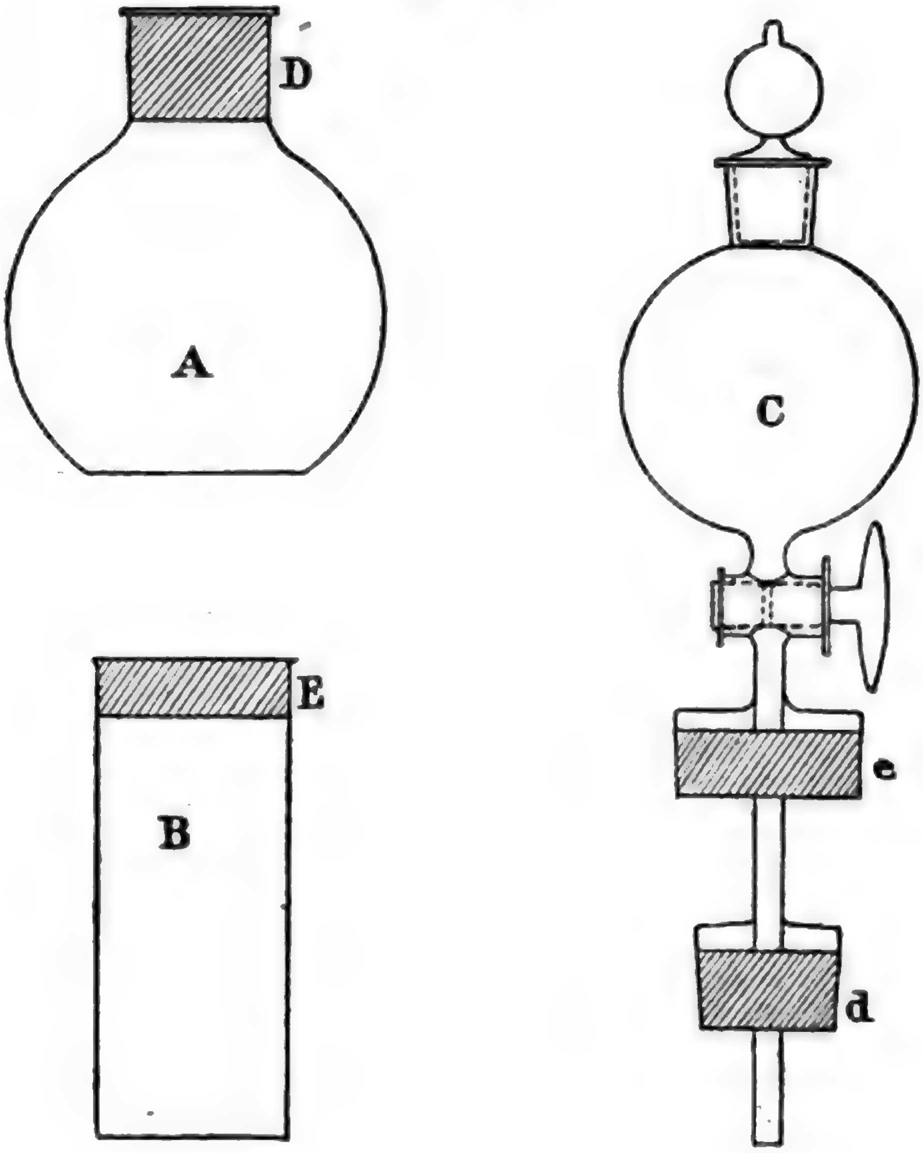
The *dihydrobromide* of 1 : 1-dimethyl-$\Delta^{2:5}$-dihydrobenzene, in which the position of the bromine atoms is doubtful, is a faintly yellow, highly refractive liquid, turning pale violet on standing, and possessing an odour of turpentine.

Action of Bromine.—The sketch on page 649 is of an apparatus which has been found to give very good results in the determination of the bromine absorption of unsaturated substances.

Into the flask *A* is placed about 30 c.c. of dry chloroform and an accurately weighed quantity (1—1·5 grams) of the substance to be tested, and the flask stoppered securely with an ordinary cork. The dropping funnel, *C*, is then attached to *B* by the ground-glass joint, *eE*, and into *C* is weighed about 25—30 grams of dry chloroform and 3—4 grams of dry bromine. *C* is then attached to *A* by the ground-glass joint *dD*, and, when the absorption is complete, is again placed in *B* and re-weighed. Any chloroform solution of bromine remaining in the stem of the funnel is prevented from escaping. Without the use of an apparatus with ground-glass joints, it is impossible to obtain accurate determinations, but the apparatus has been found to give reliable and concordant results.

A solution of dimethyldihydrobenzene (C and R) in chloroform rapidly decolorised a solution of bromine in the same solvent, and a sharp end-point was noted when one molecule of bromine had been absorbed:

FIG. 2.



1·0747 absorbed 1·6066 Br. Molecular absorption = 161·4.

C_8H_{12} requires 160 for Br_2 and 320 for Br_4.

This behaviour of the hydrocarbon was not easy to reconcile with the action of hydrogen bromide in glacial acetic acid solution, where roughly one-half of the dimethyldihydrobenzene absorbed two molecules of hydrogen bromide. It was therefore decided, having proved that bromine does not act on glacial acetic acid sufficiently rapidly to interfere with the reaction, to carry out the absorption in glacial acetic acid solution. Under these conditions, the bromine was readily absorbed, and a pale violet colour produced, which remained up to a point where the solution suddenly acquired a yellow tint, but this point is not as sharp as when chloroform is used as solvent:

1·4385 absorbed 2·3334 Br. Molecular absorption = 175 (theory = 160).

On continuing the addition of bromine, it was absorbed slowly without the evolution of the slightest trace of hydrogen bromide, and a second end-point noted when the bromine was no longer used up, the process occupying about thirty minutes:

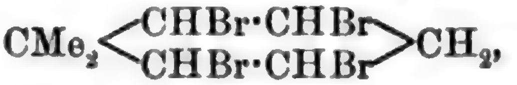
1·4385 absorbed 3·3346 Br. Molecular absorption = 250 (Br_4 = 320).

As soon as this second end-point was reached, solid commenced to separate, and, on standing for a short time, 2·1 grams were obtained, which were purified by crystallisation from light petroleum, and the bromine determined:

0·1095 gave 0·1928 AgBr. Br = 74·92.

$C_8H_{12}Br_4$ requires Br = 74·76 per cent.

2 : 3 : 5 : 6-*Tetrabromo*-1 : 1-*dimethylhexahydrobenzene*,



$$CMe_2{<}\begin{matrix}CHBr\cdot CHBr\\CHBr\cdot CHBr\end{matrix}{>}CH_2,$$

is very soluble in the cold in chloroform or benzene, and crystallises from acetone, ethyl acetate, alcohol, acetic acid, or light petroleum (b. p. 40—60°), the crystals melting without decomposition at 102°.

The authors take this opportunity of thanking Prof. W. J. Pope for the following description of the crystals.

The substance crystallises in square, transparent, colourless plates, possessing a calcite-like lustre, and belonging to the orthorhombic system; the forms present are $b\{010\}$, $c\{001\}$, and $p\{110\}$. Measurements made on two good crystals show the prism angle to be approximately 110 : 110 = 127°0′, whence the axial ratio $a : b = 2{\cdot}006 : 1$ is calculated. The crystals are soft, and show a perfect cleavage parallel to $b\{010\}$; the acute bisectrix is the axis-b, and the optic plane is $c\{001\}$. The optical axial angle is large, and the double refraction is negative in sign.

The absorption was then repeated in chloroform solution, when again a very sharp end-point was observed, the solution becoming yellow:

1·0641 absorbed 1·5762 Br. Molecular absorption = 160.

On further addition of bromine, the latter was absorbed without evolution of the slightest trace of hydrogen bromide, but so slowly that the process could only be followed by comparing the colour of the solution with that of a solution of potassium dichromate. At the end of two and a-half hours, the reaction was complete:

1·0641 absorbed 2·3213 Br. Molecular absorption = 235·6.

This result obviously means that dimethyldihydrobenzene (C and R) consists of two isomerides approximately in equal amounts, the $\Delta^{2:4}$-variety absorbing but 2 atoms of bromine, whereas the $\Delta^{2:5}$-modification absorbs 4 atoms of bromine. No solid separated from the chloroform solution, but on evaporation of the solvent, during which process no hydrogen bromide was evolved, the residue partly solidified and gave 1·6 grams of tetrabromodimethylhexahydrobenzene, melting at 102°.

An attempt was made to isolate the dibromide from the oil out of which the tetrabromo-compound had separated, by preparing a much larger quantity of material and distilling under reduced pressure. The liquid boiled for the most part at 132—133° at 22 mm., the approximate boiling point of a dibromide, but, although it passed over as a pale yellow oil, it rapidly darkened and gave off hydrogen bromide, and on exposure to air decomposed so quickly that it was quite impossible to carry out an analysis. These properties agree with those of the dibromide of dimethyldihydrobenzene (C and S) previously described (Trans., 1902, **81**, 833).

Oxidation with Potassium Permanganate.—Ten grams of the hydrocarbon were suspended in 300 c.c. of water, kept cool in ice, stirred with a turbine, and a cold 4 per cent. solution of potassium permanganate gradually added. After 700 c.c. of the oxidising agent had been used, the reaction took place so slowly that it was allowed to proceed at atmospheric temperature, and was completed when 45 grams of permanganate had been decolorised. After working up in the usual way, 6 grams of an oily residue, smelling of fatty acids, were obtained, which gradually solidified, and, after spreading on porous plate (*P*), yielded 2·5 grams of solid. Believing this to be *as*-dimethylsuccinic acid (compare Trans., 1902, **81**, 836), it was heated with acetyl chloride for two hours, the solvent evaporated, during which process 0·1 gram of crystals separated, melting at 180—185°, and crystallising from water in the characteristic slabs of crystals of dimethylmalonic acid melting at 190° with evolution of gas and the unmistakable odour of *iso*butyric acid.

The liquid residue from the crystals was distilled, when at 45 mm. all but a small amount passed over below 140°. This was proved to consist of the anhydride of *as*-dimethylsuccinic acid, by boiling with water and saturating the solution with hydrogen chloride. Needle-shaped crystals separated, melting at 140—141°, nor was this melting point altered on admixture with pure *as*-dimethylsuccinic acid.

The residue of the above distillation (0·5 gram) solidified, and, after crystallisation from water, melted at 189—190° with evolution of gas, and consisted therefore of dimethylmalonic acid.

On extracting the porous plate (*P*) with ether, 2·5 grams of an oil were obtained which showed no signs of solidification on standing. It was therefore further oxidised with potassium permanganate by heating on the water-bath, when 1 gram of *as*-dimethylsuccinic acid was isolated from the product.

Dimethyldihydrobenzene (C and S) was prepared and once more oxidised under exactly the above conditions, without, however, the isolation of a trace of dimethylmalonic acid; 6 grams of the hydrocarbon gave 1·5 grams of dimethylsuccinic acid after oxidation in the cold, and a further 0·8 gram after the second oxidation.

RESEARCH LABORATORY, PHARMACEUTICAL SOCIETY,
17, BLOOMSBURY SQUARE, W.C.

LIX.—*The Affinity Constants of Bases as Determined by the Aid of Methyl-orange.*

By VICTOR HERBERT VELEY.

DURING the past thirty years, various methods have been adopted for the purpose of assigning definite values for the affinity constants of nitrogenous bases. Such methods have consisted in determining (i) the heats of neutralisation with hydrochloric acid (Berthelot, Thomsen, Luginin, and others), (ii) the electric conductivity factors of the hydrochlorides with or without excess of either acid or base* (Walker, Bredig, Winkelblech and Lunden, and others), (iii) the catalysis of methyl acetate by the hydrochloric acid liberated by hydrolysis (Walker and others), (iv) the inversion of sucrose similarly (Walker), (v) a coefficient of extraction method (Wood and others), (vi) a coefficient of extinction method (Lellmann, associated with others), as also various methods of less importance and accuracy. A few words regarding such methods will suffice for the purpose of argument. As to (i), I have elsewhere pointed out the importance of correlating hydrolysis and thermoneutrality values, and of calculating out the latter in terms of the former by the equation proposed by

---

* The literature of the subject has been fully collated by Lunden (*Zeitsch. physikal. Chem.*, 1906, **54**, 561 *et seq.*), so it is thought necessary to give references only in special cases.

Nernst (*Zeitsch. Elektrochem.*, 1906, **12**, recommendations of the Units Commission of the Deutsche Bunsen Gesellschaft):

$$Q[_{\text{neut.}}] = RT^2{}_\epsilon \frac{d\log^{10}k}{dT} \quad . \; . \; . \; . \; . \; . \quad (1).$$

Methods (ii) to (v) will be frequently alluded to in the sequel.

As to method (vi), which was based on the subdivision of hydrochloric acid between dimethylaminoazobenzene and the several bases, applying Guldberg and Waage's equilibrium formula, it was pointed out (Arrhenius, *Zeitsch. physikal. Chem.*, 1892, **10**, 671) that the chemical system was by no means so simple as Lellmann represented, as apart from the hydrochlorides themselves, there were also present the free bases and free hydrochloric acid (or ions thereof) liberated by the process of hydrolysis. Further, the values given by Lellmann are completely at variance with those obtained by other observers and myself. It might almost appear superfluous with the great array of methods to put forward another, possibly less accurate than others previously adopted, and it is therefore incumbent upon the author to point out any advantages which it might possess. These seem to be as follows: (i) no expensive apparatus is required; (ii) several series of determinations can be made in a few minutes with the consumption of a very small amount of material, generally 0·3 to 0·8 gram; (iii) hydrolysis values can be obtained at dilutions far greater than by the electric conductivity method, which is not very trustworthy for dilutions greater than $V = 1 \times 10^4$ (V = litres/gram-equivalents) or thereabouts, even with specially wound bobbins, the introduction of condensers in the arms of the bridge, and very special precautions as to purity of water, and far greater than by chemical methods, which in concentrated solutions $V = 30$ or thereabouts require an inordinate length of time; (iv) hydrolysis values of the hydrochlorides of bases, the basic constant of which is greater than $K_b = 1 \times 10^{-9}$, can be determined, if not accurately at least within a fair approximation.

In my previous communication (Trans., 1907, **91**, 154), it was shown that, if successive quantities of 0·1 c.c. of hydrochloric acid solutions, $V = 200$ to $V = 400$, are added to a dilute solution of methyl-orange, $V = 4 \times 10^4$, the change in tint can be measured within limits (and certain values obtained) by a variable column of the same methyl-orange solution by means of a tintometer. If solutions of hydrochlorides of bases are substituted for hydrochloric acid and the process repeated similarly, other series of values are obtained, and the ratio of the latter to the former is a measure of the hydrochloric acid liberated by hydrolysis, and so of the hydrolysis value itself, as we have

$$C_{(\text{salt})}/C_{(\text{HCl})} + C_{(\text{base})} = \text{Constant} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2).$$

It will be admitted that this method is open to the criticism that the introduction of the methyl-orange as a fourth substance may tend to upset the equilibrium of the system $HCl_{(diss)} + base_{(diss)} \rightleftarrows salt_{(diss)}$, in that the liberated hydrochloric acid may combine with the azo-grouping of the methyl-orange, and that the final system containing the reddened methyl-orange (whatever its nature, or constitutions of its ions) is not identical with the initial system. But, on the one hand, such a criticism, although not previously advanced, applies equally to the catalysis of methyl acetate and inversion of sucrose methods, in both of which the final differs from the initial system, and, on the other, as will be shown in the sequel, the methyl-orange method gives results identical within the limits of experimental errors with the electric conductivity method against which no such objection can be raised.

EXPERIMENTAL.

As regards the tintometer, several minor improvements have been introduced with the view of cutting off extraneous light, whether direct or reflected. Some years' experience have shown that if daylight is used as the illuminant, the best conditions for working are at a window facing north, and on days of neither too brilliant sunshine, nor too cloudy; the worst condition, other than the impossible one of fog, is a combination of the two, namely a bright sun with heavy rain-clouds in another part of the sky.

There is, of course, always the subjective difficulty of the state of health, and other persons repeating the experiments might obtain more or less accurate results according to the appreciation of tints between red and yellow which may be considered to be within the spectrum limits of the lines Hα and D; and other persons would probably also obtain *different* values, but the *same* ratios, the latter being the really significant figures (compare Sidgwick and Moore, *Zeitsch. physikal. Chem.*, 1907, **58**, 389).

Effect of Impurities.

Effect of Impurities in Water.—The presence of carbon dioxide produced a slight alteration in colour in the diluted methyl-orange, and it was also noticed that such solution became slightly more orange when kept in loosely stoppered flasks, or when poured backwards and forwards to the tintometer cylinders, from absorption of carbon dioxide from the air.* But as the same solution was placed in both the cylinders, the presence of such carbon dioxide derived from the water or absorbed from the air was proved to be immaterial. The presence of free ammonia in water distilled from a town supply, even if it occurred, would only involve a correction less than the experimental error; the presence of albuminoses (so-called albuminoid ammonia) and the difficulty of removing the last traces of them has been alluded to in previous communications. Finally, the presence of greasy matters,* of whatever nature and however derived, produced an effect on the observations which can best be described as inhibitory or poisonous. It was found that water distilled from a town supply to which were added 10 c.c. of a concentrated solution of potassium permanganate and 20 c.c. of $N/20$ sulphuric acid was of a sufficient degree of purity for the purpose of this investigation.

---

* The coloration of methyl-orange by carbonic acid was first observed by Kuster (*Zeitsch. anorg. Chem.*, 1897, **13**, 136).

Effect of Glass.—The same measuring vessels, flasks and pipettes, were always used for the same purpose, but the glass of the tintometer cylinder was affected by the kind of solution used. Thus, if experiments were conducted with a solution but slightly hydrolysed following upon another solution hydrolysed to a considerable degree, too high results were at first obtained and vice versa, a result in accordance with former experience in density determinations. The commonly suggested remedy of cleansing with hydrochloric acid and then steaming out is clearly inadmissible in this case, and the better alternatives were adopted of either having the tubes filled with the methyl-orange solution between each set of experiments or, preferably, of working with similar solutions in succession and rejecting the first or even second set of observations whenever a change becomes necessary,

It was shown in my previous paper that if V is the concentration of the hydrochloric solution when added to the methyl-orange solution at the time of the first observation, namely, $V_{(HCl)} \times 10 \times 20$, and X the number of units of 0·1 c.c. added (V/X being the consequent dilution) and y the height of the variable tintometer column, then

$$y \overset{\dagger}{=} kX - b \qquad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (3),$$

wherein k is the important factor correlating y and x.

It was further pointed out that the factor b arises from some initial period, caused either by the so-called chemical inertia, or more probably by albuminoses retained in the water or impurities on the surface of the glass. Subsequent experience showed that the greater the care taken to eliminate such impurities the less such an initial period and the more b becomes a vanishing quantity. Hence the one or two irregular observations obtained at the outset have been neglected as inconsequent, and the starting point of the reaction or, geometrically, the origin of co-ordinates is taken to be that at which the reaction confirms to the equation :

---

* These have been variously attributed to lubricating agents in stills (Ostwald) or to substances extracted from rubber corks or tubing (Manley), but I see no reason for altering my view that a main cause is the slime of certain bacteria, the constituents of which may volatilise with the steam, although the bacteria themselves may have long disappeared.

† It is unfortunate that the symbol x, applied to the abscissæ of the Cartesian system of co-ordinates, should also have been applied to the portion of a salt hydrolysed; to avoid confusion, the capital letter has been adopted for the former.

$$y = kX \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 3(bis).$$

If the hydrochloride of a base be substituted for the acid itself, then

$$y' = k'X \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4).$$

Dividing equation (4) by (3) as X is identical, we have

$$y'/y = k'/k = \text{Hydrolysis} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5),$$

or, in other words, successive increments of chemical change are measured in terms of successive increments of lengths, which would be an ideal state of affairs if the human eye were an optical instrument of precision and daylight a perfect illuminant.

The experiments with the hydrochloric acid solutions $V = 8 \times 10^4$, 6×10^4, and 4×10^4 have been repeated several times under various conditions; the values of k obtained for the two former have been multiplied up in terms of the last; the mean value of all calculated out by the method of least squares, using Bessel's function, works out at $k = 3{\cdot}2 \pm 0{\cdot}13$, and on reduction the values are as under :

V	8×10^4	6×10^4	4×10^4
k............	1·6	2·4	3·2

These are used in the sequel as standard factors.

But in the case of bases the hydrochlorides of which are but little hydrolysed, solutions of greater concentration as regards the hydrochloric acid, free or combined, were required in order to obtain determinations ; in such cases, the above factors were multiplied up proportional to such concentration. It is, of course, true that hydrolysis values and basic constants thus obtained are only *indirectly* deduced, and not *directly* determined ; an objection may also be raised that the ion-concentrations of the methyl-orange and of the salt are unequal. Such an objection is valid, but if this necesssary condition were fulfilled no determinations would be possible as the intensity of colour of the methyl-orange would be too great to observe slight variations of tint.

But, however this may be, it will be shown in the sequel that such values are in accordance with those obtained by the conductivity method, so that such approximations may be regarded as fairly satisfactory. But, in such cases, it was found that only a few observations were possible, since some condition of equilibrium setting in, further additions of the solutions of the hydrochlorides produced no further alteration of tint.

The Salts and Solutions Used.

Most of the salts were purchased from reliable firms, and, if necessary, were purified by one or more recrystallisations, generally from water; other samples, of a great degree of purity, were presented by numerous friends, to whom collectively I have here to tender my thanks, but they will be alluded to individually in the course of the text. I have also to express my obligations to the Research Fund Committee of the Chemical Society for a grant towards the purchase of the more expensive materials.

Solutions were made up so as to contain, unless otherwise stated, the molecular weight of hydrochloric acid, or 1 gram hydrogen ion, in $V = 20$ ($N/20$ solutions); these were allowed to stand for a few hours, and then diluted to $V = 200$, &c. Such diluted solutions were allowed to stand overnight (eighteen hours or thereabouts), as experience showed that in many cases this time was required before the final equilibrium of the system water-salt-acid-base was reached.

The observations and calculations for one set of experiments only are set out as explanatory of the above text, the case of *o*-toluidine hydrochloride being selected. The number of successive portions X of 0·1 c.c. of the hydrochloride are given in column I; in II, the actual tintometer scale-readings in cm.; in III, the values of y' thus observed; in IV, the calculated values of y', $K = 0{\cdot}65$, and in V the values of y, corrected, of hydrochloric acid of same original concentration as to hydrogen ions:

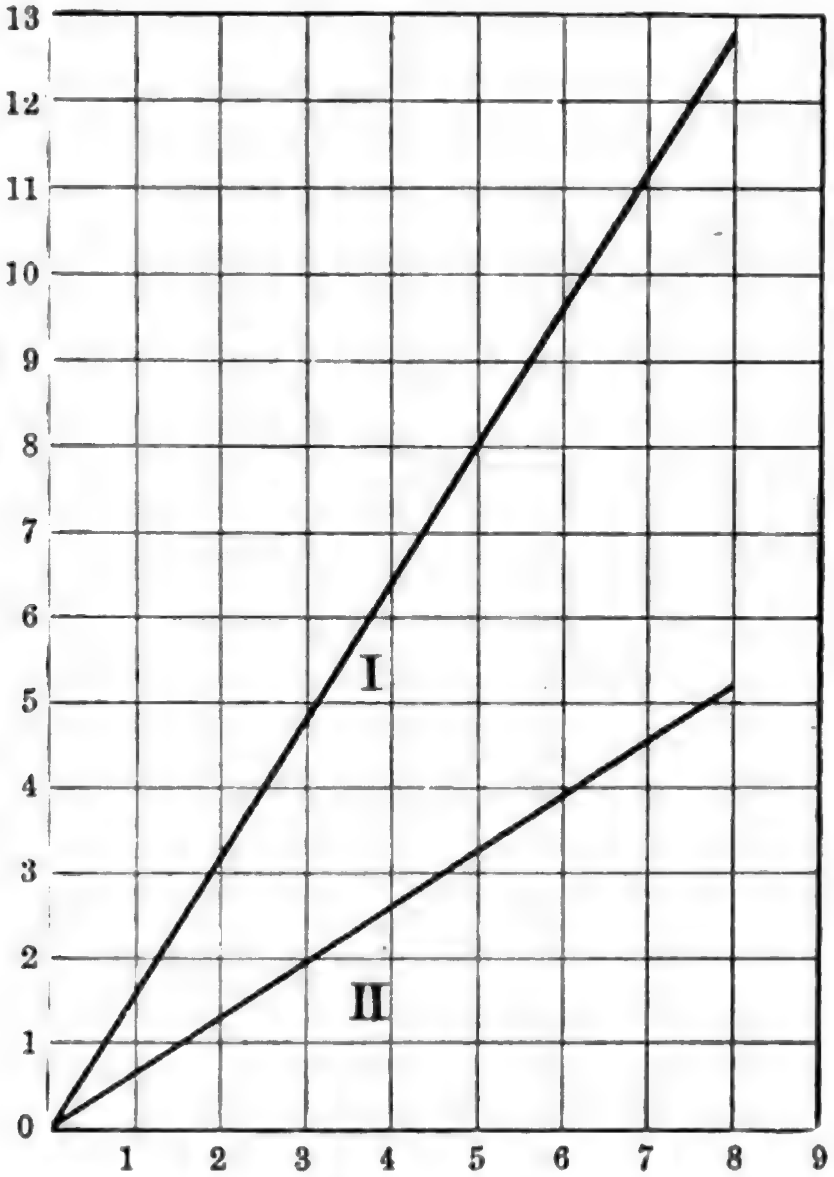
o-*Toluidine Hydrochloride*, $V = 8 \times 10^4$. Temperature = 12°.

I.	II.	III.	IV.	V.
—	8·0	—	—	—
1	8·7	0·7	0·65	1·6
2	9·2	1·2	1·3	3·2
3	9·9	1·9	1·95	4·8
4	10·6	2·6	2·6	6·4
5	11·2	3·2	3·25	8·0
6	11·8	3·8	3·9	9·6
7	12·6	4·6	4·55	11·2
8	13·2	5·2	5·2	12·8

If any number in column IV is divided by the corresponding number in the same horizontal line in column V, that is, y/y' or $k/k' = 0{\cdot}406$, or, in other words, at the dilution given above, 40·6 per cent. of the *o*-toluidine hydrochloride is hydrolysed into the free base and hydrochloric acid. The graphs for the salt and acid are given in the figure.

In the sequel, only the numbers corresponding with column III will be given, namely, the values of y' and also k', the numbers of columns I, II, and V being taken to be understood, whilst those of IV can be readily calculated without repetition of figures, often identical.

FIG. 1.



Ordinates represent the heights in centimetres of the variable methyl-orange column, abscissæ unit volumes added.
I. *Hydrochloric acid.* II. o-*Toluidine hydrochloride.*

Determination of Affinity Constants.

From the hydrolysis values, the affinity constants of the bases can be calculated by Arrhenius' formula

$$\frac{k_b}{k_w} = \frac{(1-x)V}{x^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6),$$

in which k_b is the affinity constant of the base, k_w the product of concentration of ions of water, V dilution in litres/gram-equivalents,

x the proportion per equivalent of salt hydrolysed, and $1-x$ the proportion not so hydrolysed. The values of k_w within the range of temperature used are taken from the tables of Kohlrausch and Heydweiler (*Ann. Phys. Chem.*, 1894, [iii], **53**, 214):

Temp.	10°	15°	25°
k_w	$0{\cdot}31\ 10^{-14}$	$0{\cdot}49\ 10^{-14}$	$1{\cdot}11\ 10^{-14}$

those for intermediate temperatures being taken out by graphical interpolation, which is probably sufficiently accurate for the present purpose. Thus, to take the example of *o*-toluidine hydrochloride given above, since the same value, 0·406, was obtained with a solution $V = 1 \times 10^4$ as with $V = 8 \times 10^4$, a point which will be considered later, we have, taking k_w at 12°, the temperature of observation $= 0{\cdot}37\ 10^{-14}$:

$$\frac{k_b}{0{\cdot}37\ 10^{-14}} = \frac{(1-0{\cdot}406)1\times10^4}{(0{\cdot}406)^2} \quad \therefore \quad k_b = 1{\cdot}34\ 10^{-10} \text{ at } 12^\circ.$$

The values of k_b calculated from Bredig's determinations (electric conductivity method, *Zeitsch. physikal. Chem.*, 1894, **13**, 322), $= 3{\cdot}2\ 10^{-10}$ at 25°, and from Walker's determinations (inversion of sucrose method, Trans., 1895, **67**, 576), $= 10{\cdot}9\ 10^{-10}$ at 60°, are of a similar order; the values for a mean straight line being $(1{\cdot}1,\ 3{\cdot}6,\ \text{and}\ 10{\cdot}7)10^{-10}$ respectively.

Bases not containing an Alkyl Grouping.

Hydroxylamine Hydrochloride.—Solutions of two concentrations were examined, in both cases all reaction soon coming to an end; the results were as follows (temperature 15°):

$V = 2 \times 10^4$.	$V = 1 \times 10^4$.
0·5	1·2
0·9	2·4
0·9	3·3

Values of $k = 0{\cdot}5$ and 1·15, corrected 0·53 and 1·07; hydrolysis value = 8·1 per cent., $k_b = 6{\cdot}5\ 10^{-9}$ at 15, $V = 1 \times 10^4$. Winkelblech (*Zeitsch. physikal. Chem.*, 1901, **36**, 574) found a hydrolysis value 2·5 per cent. at $V = 1024$, temperature = 25°, which gives $k_b = 7{\cdot}35\ 10^{-9}$. These numbers are fairly concordant, especially as Winkelblech admitted that hydroxylamine was too strong a base to give satisfactory hydrolysis values by the electric conductivity method.

Hydrazine Hydrochloride.—Three series of experiments were conducted with concentrations $V = 4 \times 10^4$ and 8×10^4; in the two of them (series I and II), the original $V = 20$ solution was diluted directly to $V = 2$ and $4\ 10^2$; in the third (series III), the original solution was heated for three hours at a temperature of 60° in a thermostat and then diluted to $V=2\times10^2$. The following results were obtained (temperature 15°):

Series I. $V=8\times10^4$.	Series II. $V=4\times10^4$.	Series III. $V=4\times10^4$.	Series I. $V=8\times10^4$.	Series II. $V=4\times10^4$.	Series III. $V=4\times10^4$.
0·6	1·2	1·6	2·9	6·1	8·3
1·2	2·5	3·3	3·5	7·4	10·1
1·8	3·6	5·0	4·1	7·4	10·1
2·4	4·8	6·5	4·7	7·4	10·1

Values of $k=0·6$, 1·2, and 1·67; hydrolysis value for I and II = 37·5, for III, 51·5.

As regards the above determinations, two points require comment: firstly, the hydrolysis is not completed when the original solution is kept at the ordinary temperature, and secondly, the differences $y'-y$, although approximately constant and conforming to the straight line formula, yet show a slight tendency to increase with the number of observations. A similar phenomenon in the case of dicarboxylic acids has been noticed in the methyl-orange method (*Zeitsch. physikal. Chem.*, 1906, **57**, 159), as also by Ostwald in the conductivity method (*ibid.*, 1889, **3**, 380). The cause of the phenomenon, whether in the case of diacidic bases or dibasic acids, is probably the same. Bredig (*ibid.*, 1894 **13**, 314) showed that in concentrations varying from $V=32$ to $V=1024$ hydrazine hydrochloride is hydrolysed very approximately into the mono-hydrochloride and hydrochloric acid, thus:

$$ClH_3N\cdot NH_3Cl + H\cdot OH = ClH_3N\cdot NH_3\cdot OH + HCl,$$

that is, the hydrolysis value = 50 per cent.

My experiments with the heated solution with $V=4\times10^4$, a dilution forty times greater, gave the value = 51·5 per cent. It therefore appears that in the case of hydrazine hydrochloride, and as will be shown on other diacidic bases, Arrhenius' dilution law is not applicable; no value of k_b can therefore be deduced. Hydrazine is further remarkable in that the introduction of an amino-group (attached to a nitrogen atom) in ammonia *decreases* the basic value, whereas in all other cases the amino-group thus introduced increases the basic value. Bredig (*loc. cit.*) suggests that this result is correlated with the contiguity of the amino-groups.

Guanidine Hydrochloride.—Observations were made with two different concentrations with the following results:

$V=2\times10^4$.	$V=4\times10^3$.	$V=2\times10^4$.	$V=4\times10^3$.
0·2	1·2	0·9	5·9
0·5	2·5	0·9	7·3
0·9	3·6	0·9	8·6
0·9	4·7		

Values of $k=0·25$ and 1·2, corrected 0·245 and 1·25; hydrolysis value = 3·7 per cent., value of $k_b=1·1\ 10^{-8}$, at $V=4\times10^3$, temperature

15° ; no value of guanidine has as yet been given, owing to irregularities of results.

Aminoguanidine Hydrochloride.—No hydrolysis could be detected, which serves as a good illustration of the increase of a basic constant by the effect produced by the substitution of hydrogen in guanidine by an amino-group attached to a nitrogen atom.

Carbamide Hydrochloride.—The hydrolysis value and basic constant of carbamide has been so frequently determined that it was not thought necessary to add to the determinations.

Semicarbazide Hydrochloride.—The salt (presented by Mr. N. V. Sidgwick) was purified by recrystallisation. Solutions of the concentrations were examined, but all reaction soon came to an end. The following results were obtained (temperature 15°):

$V=4\times10^4$.	$V=2\times10^4$.	$V=4\times10^4$.	$V=2\times10^4$.
0·35	0·6	1·4	2·0
0·7	1·4	1·7	2·0
1·0	2·0		

Values of $k=0{\cdot}35$ and $0{\cdot}7$; hydrolysis value = 11 per cent. ; value of k_b at $V=2\times10^4=9{\cdot}1\ 10^{-9}$. Wood (Trans., 1903, **83**, 571), by the methyl acetate catalysis method, found a hydrolysis value = 10·4 per cent., $V=10$, which gives a basic constant $2{\cdot}7\ 10^{-11}$ at 40°, making semicarbazide a much weaker base. But whichever of the discrepant results may be correct, the effect of the substitution of hydrogen in carbamide by an amino-group attached to a nitrogen atom is similar to that observed in the above cases of guanidine and aminoguanidine.

Aliphatic Amines.

The hydrochlorides of methylamine, ethylamine, triethylamine (samples of which were kindly presented by Mr. N. V. Sidgwick), *iso*propylamine, and trimethylamine were examined by this method, but only traces of hydrolysis could be detected in the last case. This result is in accordance with Bredig's determinations by the electric conductivity method, the value of the basic constant for the last-named base, namely, $k_b=7{\cdot}4\ 10^{-3}$, being lower than those of the others.

Ethylenediamine Hydrochloride.—Only one solution was examined, namely, the original $V=20$, giving on addition to the methyl-orange $V=4\times10^3$; all reaction soon came to an end. The results were as follows :

$V=4\times10^3$.	Temp. 16°.
0·2	0·8
0·4	1·0
0·6	1·0

Value of $k=0{\cdot}2$; assuming that of hydrochloric acid of the same dilution to be 32, the hydrolysis value = 0·6 per cent., and the value of $k_b = 5\cdot9\ 10^{-7}$.

Bredig (*loc. cit.*) remarked that this salt shows no appreciable acid reaction with methyl-orange, without giving details of the strength of the solutions, and that this salt is hydrolysed by water quite inappreciably, an observation in accordance with the above results, which are only put forward as an approximation.

β-Methylhydroxylamine Hydrochloride.—This salt gave a hydrolysis value of 3 per cent. with $V = 4 \times 10^3$, but, as it was found possible to obtain only a few results, no conclusions are drawn therefrom.

Aminocarboxylic Acids.

In my former paper, certain values of k were given for glycine and betaine hydrochlorides which were only compared with those of hydrochloric acid; these values, corrected and recalculated as explained in the introduction, give for the hydrolysis numbers, glycine hydrochloride = 86·0 per cent., and betaine hydrochloride = 94·7 per cent. Subsequently, results have been obtained for the hydrochlorides of glycine ethyl ester, sarcosine, and leucine.

Glycine Ethyl Ester Hydrochloride.—Two sets of determinations were made with relatively concentrated solutions, as the hydrolysis was very slight; the results are given as under (temperature 18°):

$V = 2 \times 10^3$.	$V = 1 \times 10^3$.	$V = 2 \times 10^3$.	$V = 1 \times 10^3$.
0·3	0·6	1·8	3·0
0·7	1·2	1·8	3·6
1·1	1·7	1·8	4·2
1·5	2·3		

Values of $k = 0\cdot35$ and $0\cdot6$, corrected $0\cdot32$ and $0\cdot65$; assuming the values of hydrochloric acid at these concentrations to be 32 and 64 respectively, the hydrolysis number = 1 per cent. Value of k_b ($V = 2 \times 10^3$) $= 9\cdot7\ 10^{-8}$. Johnson (*Proc. Roy. Soc.*, 1906, **78**, *A*, 96) was unable to obtain a value of the basic constant of the above substance by the methyl acetate catalysis method, as the reaction proceeded too slowly. Walker (*ibid.*, 148) remarks thereon that esterification greatly increases the value of the basic constant, probably by breaking up the ring-formation.

The following numbers, although not strictly comparable owing to differences of temperature, may be of interest as illustrating the above point:

Glycine.	Glycine methyl ester.	Glycine ethyl ester.
$k_b = 2\cdot66\ 10^{-12}$ at 25°	$220\ 10^{-12}$ at 40°	$97000\ 10^{-12}$ at 15°

Sarcosine Hydrochloride.—Two concentrations were worked with, giving the following results (temperature 12°):

$V=8\times10^4$.	$V=4\times10^4$.	$V=8\times10^4$.	$V=4\times10^4$.
1·2	2·9	8·1	14·6
2·5	5·9	9·5	14·6
3·8	8·8	10·9	14·6
5·2	11·7	12·3	14·6
6·7	14·6		

Values of $k=1·35$ and 2·9, corrected 1·4 and 2·8; hydrolysis value $=87·5$ per cent.

Leucine Hydrochloride.—Conditions as in the case of the above:

$V=8\times10^4$.	$V=4\times10^4$.	$V=8\times10^4$.	$V=4\times10^4$.
1·3	2·8	6·8	13·7
2·6	5·8	8·1	13·7
4·1	8·4	9·3	13·7
5·4	11·0	10·7	13·7

Values of $k=1·35$ and 2·75, corrected 1·36 and 2·73; hydrolysis value $=84·3$ per cent.

Winkelblech (*loc. cit.*) either directly determined or calculated out the hydrolysis values of these hydrochlorides of aminoacetic acids from the results of Bredig (*loc. cit.*) and Carrara and Rossi (*Atti R. Accad. Lincei*, 1897, **6**, 219). His results and those given above compare as follows:

	Winkelblech. $V=1024$. Temp. 25°.	Veley. $V=4\times10^4$ to 8×10^4. Temp. 12° or 15°.
Glycine	86·0 per cent.	83·6 per cent.
Sarcosine	87·5 ,,	88·6 ,,
Betaine	94·6 ,,	94·7 ,,
Leucine	85·3 ,,	84·3 ,,

The agreement of results obtained by two totally different methods at different concentrations appears very satisfactory; the greatest variation, about 3 per cent., occurs in the case of glycine, but, adopting Winkelblech's constants, a hydrolysis value of 86 per cent. could have been obtained at $V=1316$, whereas the greatest dilution examined by him was $V=1024$.

Since from the above results nearly identical hydrolysis values have been obtained by Winkelblech at $V=1024$, say, $V=1\times10^3$, and by myself at $V=4\times10^4$ and 8×10^4, or forty and eighty times the dilution, then one might conclude that in the Arrhenius equation, $k_b/k_w=(1-x)V/x^2$, the right-hand side of the equation cannot be summed to infinity (condition $1-x=o, V=\infty$), but that there is a limiting value of V at which the equation Hydrochloride + Water $\rightleftarrows$ Base + Acid (or ions thereof) becomes reversible.

Drucker (*Zeitsch. Elektrochem.*, 1907, **13**, 81) has recently put forward the view that the ultimate limit of ionic dissociation is reached completely in the case of salts containing univalent ions, and nearly completely in those containing bivalent ions, at a dilution

$V = 1 \times 10^4$, hydrolysis, *inter alia*, causing error. But this view has been criticised by Kohlrausch (*ibid.*, 336), who, whilst admitting that the electric conductivity method is not trustworthy beyond this dilution, yet shows by extrapolated curves that the ionic dissociation at such dilution falls short by 1 to 8 per cent. of its final value. My observations by the methyl-orange method, of which only a few are given in the present communication, are in accordance with Drucker's view, since in by far the larger number of cases a limiting value is reached at the dilution $V = 1 \times 10^4$, or at most, 2×10^4. But a conclusion could only be regarded as final if the methyl-orange or traces of impurities in either the water or the salts were not possible disturbing factors. The present state of affairs cannot be better summed up than in the following passage, "the last words regarding dilute acids or bases cannot be spoken until one has succeeded in examining their solutions in pure water" (Kohlrausch, *loc. cit.*, 646).

Uric Acid Derivatives.

For the sake of convenience, these substances are considered here as ureides and closed-chain compounds analogous to betaine.

Caffeine Hydrochloride.—The sample of this salt, purchased from Merck, was in the form of large crystals, and the very slight efflorescence of caffeine on their surface was removed before dilution. The course of events on adding water can readily be followed; firstly, the water removes the hydrochloric acid, and secondly, the separated caffeine slowly dissolves, probably as hydroxide.

As it was stated some years ago by Schmidt (*Annalen*, 1883, **217**, 284) that this salt is completely decomposed both by water and alcohol into the free base and hydrochloric acid, solutions in both these media were examined.

The results obtained with aqueous solutions, temperature 15°, were as follows:

$V = 8 \times 10^4$.	$V = 4 \times 10^4$.	$V = 8 \times 10^4$.	$V = 4 \times 10^4$.
1·6	2·9	6·3	12·5
3·1	6·0	7·9	15·7
4·7	9·0	9·5	15·7

Values of $k = 1·55$ and $3·1$; hydrolysis value $= 97·2$ per cent. Wood (Trans., 1903, **83**, 571) found a hydrolysis value $= 89·7$ per cent. at $V = 10$, temperature $= 40°$, which gives $k_b = 4·1\ 10^{-14}$; substituting these last numbers in the Arrhenius equation, the value of V, corresponding with hydrolysis 97·2, is 28·5 at 40°, and probably about 188 at 15° ($k_{w15} : k_{w40} = 1 : 6·6$). This may therefore be regarded as the limiting value of V.

Alcoholic Solution.—The salt was dissolved in alcohol (99·5 per cent.

per volume), which had been specially purified for another purpose from traces of impurities other than water, so as to obtain a $N/20$ solution as customary; this process was very tedious, and required several hours and a gentle heat for completion. The solution thus obtained was diluted with the same alcohol so as to give a $N/200$ solution, which was used for the purpose of observations:

$V=4\times10^4$.		$V=4\times10^4$.	
2·4	7·0	11·6	16·4
4·8	9·3	14·0	18·7

Hydrolysis value = 73·4 per cent.

It is, of course, true that hydrolysis might have resulted, and probably did result, from the water of the methyl-orange solution, but to meet the argument that the alcohol inhibited the full reaction of the indicator, experiments were repeated with betaine hydrochloride under precisely similar conditions; the values so obtained were identical within the limits of experimental error with those with the aqueous solution. The above results, although not conclusive, yet appear sufficient to show that caffeine hydrochloride is not completely decomposed by alcohol into the free base and acid as stated by Schmidt.

Theobromine Hydrochloride.—Owing to the sparing solubility of the base, the method of procedure was altered; the salt was dissolved directly to give a $N/400$ solution; even under these conditions the separated theobromine dissolved very slowly, and it was found necessary to warm the solution. One series of experiments was conducted with the following results:

$V=8\times10^4$.		$V=8\times10^4$.	
1·3	3·9	6·6	8·9
2·6	5·2	7·7	10·4

Value of $k=1·3$; hydrolysis value = 81·2 per cent.

Wood (*loc. cit.*) gave an approximate value 73 per cent. in an $N/10$ solution, this number being arrived at by the indirect solubility method; the value of k_b deduced is $1·65\ 10^{-13}$ at 40°, and, making the substitutions as explained in the case of caffeine, the value of V for a hydrolysis 81·2 per cent. is 28, and at 15° about 185.

The general agreement of my results with those of Wood for caffeine and theobromine is very satisfactory, although here again they point to a limiting value of V in the Arrhenius equation.

Summary.

(I) The method of determining the hydrolysis values of the hydrochlorides of nitrogen-containing bases, and hence the affinity constants of the latter, by means of the methyl-orange method is described in detail.

Google

(II) The relative advantages of the method, possibly not so accurate as other methods previously proposed, are discussed, and certain obvious criticisms are considered.

(III) Results are given for the hydrochlorides of (i) bases not containing an alkyl grouping, (ii) aliphatic amines, (iii) aminoacetic acids, and (iv) uric acid derivatives.

As regards hydrazine in (i) and in all cases of (iii), it is shown that the results obtained by the methyl-orange method are concordant with those obtained by the electric conductivity method, although the dilutions used were forty to eighty times greater. The conclusion, although not considered final, drawn therefrom is to the effect that the hydrolysis reaction becomes reversible when a certain dilution is attained.

As regards cases of (iv), the general agreement of the results obtained by the methyl-orange method with those of the solubility method is considered, although the increase of hydrolysis relative to dilution is less than that required by the Arrhenius formula.

In a subsequent communication, it is proposed to give an account of results obtained by the methyl-orange method for the hydrochlorides of bases derived from cyclic compounds.

LX.—*Traces of a New Tin-group Element in Thorianite.*

By Clare de Brereton Evans.

In the course of an examination of the iron residues separated from 5 cwt. of the cubical Ceylon mineral belonging to Sir William Ramsay (compare O. Hahn, *Proc. Roy. Soc.*, 1905, **76**, *A*, 115; Dunstan and Blake, *ibid*, 760), it was found that about 1 per cent. of the material was formed of sulphides of the silver, copper, and tin-group elements which had escaped precipitation in the proper place.

A preliminary examination showed this sulphide precipitate to be mainly due to lead, of which thorianite contains nearly 3 per cent. as oxide (Dunstan and Jones, *ibid.*, **77**, *A*, 546, and others); the rest, about 10 per cent. of the sulphides as it proved, was a mixture of sulphides of the copper and tin metals which are found only as traces in the mineral itself (Büchner, *ibid.*, **78**, *A*, 358).

During the separation of these sulphides into groups in the ordinary course of analysis colorations were observed which could not be accounted for and, since further inquiry led to the conclusion that these colorations were due to some substance associated with the tin metals, an examination of the thorianite residues containing this group was determined on.

The material used in the investigation amounted altogether to about 2·5 kilos. of mixed sulphides; 1 kilo. of this was laboriously collected from 80 kilos. of the iron residues as already indicated (this was particularly rich in tin-group sulphides), and the rest was part of the lead residues of the 5 cwt. of thorianite. Rather more than 6 per cent. of the whole proved to be sulphides of the tin group; this was separated with sodium hydroxide by fusion in a nickel crucible. A portion of the 150 grams so obtained was analysed, but, although only arsenic, antimony, tin (stannic), and selenium were detected, it was evident from the colour of the filtrates that some soluble brown sulphide (?) was also present, and search was made for a method of separation.

Eventually this brown sulphide was isolated with arsenious sulphide, which it resembles in being insoluble in hydrochloric acid and readily soluble in ammonium carbonate solution; to the latter it gives a characteristic deep brown colour. Like arsenious sulphide it dissolves in nitric acid but the concentrated syrupy liquid has a strong golden-brown colour, and leaves on evaporation at 120° a brown, hygroscopic oxide; this is reduced by hydrogen at 250—300° to a black oxide and then at a higher temperature to a dark grey, non-volatile metal which melts at a bright red heat.

The brown sulphide is attacked only with difficulty by a mixture of hydrochloric acid and potassium chlorate; after this treatment the greater part remains mixed with sulphur, from which it is easily removed by a solution of ammonium carbonate.

After many months of work only about 0·05 gram of the brown oxide has been collected from about one-third of the mixed sulphides and this is not free from arsenic. This corresponds with about 1 part in 1·5 million (less than 1 gram to the ton) of thorianite or 0·005 per cent. of the tin-group sulphides, an amount which would very likely have escaped notice altogether had it not been that the sulphide dissolves in water, which is coloured brown by a very small quantity. This solubility in water greatly increases the difficulty of separation, for the solid is not easily recovered from what appears to be a true and not a colloidal solution; it accounts also for the fact that hydrogen sulphide and acid only partly re-precipitate the sulphide from solutions containing ammonium carbonate.

The determination of the equivalent of the metal has been attempted in two ways: by electrolysis, using Faraday's Law, and by reduction of the brown oxide to metal by heating in hydrogen; the latter method indicates a considerably higher equivalent than that of arsenic.

The electrolysis of a few milligrams of material was carried out with the help of Dr. Brill, who weighed the small platinum electrodes on his balance of the Nernst type. The same current was used to deposit antimony, bismuth, and the unknown element from similar solutions of their chlorides containing gelatin, the standard being silver deposited from a solution of silver perchlorate. There was not more than about 1 per cent. of error in the equivalent found for antimony by this method but the deposit of the unknown element was unsatisfactory.

A preliminary spectroscopic examination revealed no new lines, but it is hoped to make further experiments in this direction.

Incidentally a little more knowledge of the composition of thorianite has been gained. It is now possible to state positively that it contains arsenic, mercury, bismuth, molybdenum, and selenium; several grams of arsenious sulphide have been isolated, and a drop of mercury weighing about 0·5 gram; bismuth, molybdenum, and selenium are present in much smaller amount. The lead residues contain also a quantity of silica, but this may have found its way in from vessels employed in the disintegration of the mineral, although the method used (fusion with bisulphate) scarcely warrants this assumption.

Incidentally also a new triple *oxalate* of thorium, uranium, and ammonium was prepared in considerable quantity. To obtain this the pale green double oxalate formed by adding oxalic acid to a solution containing thorium and a uranous salt was dissolved in ammonium oxalate solution and the solution was then slowly evaporated; it forms large emerald-green crystals which lose ammonia and water on exposure to air. The composition of these crystals, determined in conjunction with Miss K. A. Burke, appears to be $ThU_25(NH_4)_2(C_2O_4)_{10},14H_2O$.

Lack of material has for the time brought the investigation to a close, but steps are being taken to continue the search for the supposed new element in other ores of arsenic.

CHEMISTRY LABORATORY,
UNIVERSITY COLLEGE.

LXI.—*The Triazo-group. Part II. Azoimides of Propionic Ester and of Methyl Ethyl Ketone.*

By MARTIN ONSLOW FORSTER and HANS EDUARD FIERZ.

WITH the object of investigating more closely the effect produced on a triazo-group by the immediate neighbourhood of carbonyl, we have compared the properties of the α- and β-triazo-derivatives of propionic ester, $CH_3·CHN_3·CO_2·C_2H_5$ and $N_3·CH_2·CH_2·CO_2·C_2H_5$, substances prepared from the corresponding halogen derivatives and sodium azide. The comparison has brought out the point foreshadowed by previous experiments. α-Triazopropionic ester may be hydrolysed by alcoholic potassium hydroxide without losing nitrogen, and the acid has been isolated in crystalline form; with considerable excess of alkali, decomposition occurs even more readily than in the case of triazoacetic acid, and, although we have not isolated pyruvic acid, the occurrence of ammonia in the liberated nitrogen indicates that action follows the course pursued by the lower homologue and by camphorylazoimide (Trans., 1905, **87**, 826):

$$CH_3·CHN_3·CO_2H \longrightarrow N_2 + CH_3·C(:NH)·CO_2H.$$

Hydrazoic acid is not eliminated, whereas β-triazopropionic ester loses its nitrogen in that form so readily that the amide is not produced when the substance is shaken with aqueous ammonia, whilst potassium hydroxide, aqueous or alcoholic, gives no trace of nitrogen:

$$N_3·CH_2·CH_2·CO_2·C_2H_5 \longrightarrow HN_3 + CH_2:CH·CO_2H + C_2H_5·OH.$$

It would have been interesting to compare, from the same standpoint, the structurally different triazo-derivatives of methyl ethyl ketone, $CH_3·CO·CHN_3·CH_3$ and $CH_3·CO·CH_2·CH_2·N_3$, but the chloroketone corresponding to the latter is not available, and we have chlorinated methyl ethyl ketone many times without obtaining it. 3-Triazobutanone-2 and 1-triazobutanone-2, however, are described in this communication, and both resemble closely the triazo-derivative of acetone in respect of their behaviour towards alkali, the percentage of nitrogen set free being 4 per cent. less than two-thirds from the "internal" azoimide, whilst the deficit is 2·5 per cent. in the case of the "external" derivative. The remaining nitrogen being eliminated in the form of hydrazoic acid and ammonia, it is probable that the hydroxy-ketone is produced in association with the mono-imine of the diketone, as indicated by the following equations:

A. I. $CH_3·CO·CHN_3·CH_3 = CH_3·CO·C(:NH)·CH_3 + N_2.$
II. $CH_3·CO·C(:NH)·CH_3 + H_2O = CH_3·CO·CO·CH_3 + NH_3.$
III. $CH_3·CO·CHN_3·CH_3 + H_2O = CH_3·CO·CH(OH)·CH_3 + HN_3.$

B. I. $N_3\cdot CH_2\cdot CO\cdot CH_2\cdot CH_3 = N_2 + NH\colon CH\cdot CO\cdot CH_2\cdot CH_3$.
II. $NH\colon CH\cdot CO\cdot CH_2\cdot CH_3 + H_2O = NH_3 + O\colon CH\cdot CO\cdot CH_2\cdot CH_3$.
III. $N_3\cdot CH_2\cdot CO\cdot CH_2\cdot CH_3 + H_2O = HN_3 + HO\cdot CH_2\cdot CO\cdot CH_2\cdot CH_3$.

The separation of hydrazoic acid, taking place in subordination to the removal of nitrogen, has now been observed in the case of five α-triazoketones, which are thereby distinguished from triazocamphor; the circumstances which encourage this secondary change have been already indicated (this vol., page 73), and from the fact that 3-triazobutanone-2 is more soluble in very dilute alkali than in water, and is not removed from such a solution by ether, we suggest that the operating cause of the change in question is enolisation. This particular form of molecular rearrangement would so modify the environment of the triazo-group that the possibility of developing the unstable ring-system, already indicated, would no longer present itself. Enolic forms of triazoacetone and of 1-triazobutanone-2, namely,

$$N_3\cdot CH\colon C(OH)\cdot CH_3 \text{ and } N_3\cdot CH\colon C(OH)\cdot CH_2\cdot CH_3,$$

would be unsaturated triazo-alcohols, whilst the corresponding isomeride of 3-triazobutanone-2 would suggest analogy to ethyl triazoformate,

$$CH_3\cdot C(OH)\colon CN_3\cdot CH_3 \text{ and } O\colon CN_3\cdot O\cdot C_2H_5,$$

from which the total nitrogen is eliminated in the form of hydrazoic acid (this vol., page 81).

One of the points which the azoimides of these elementary aliphatic types have brought into prominence is the great depression in osmophoric effect exerted by the triazo-group as compared with the result of introducing this complex into the aromatic nucleus. Previous workers have noticed that replacement of hydrogen by the triazo-group in benzenoid compounds has usually resulted in the development of a characteristic odour; Rupe and von Majewski (*Ber.*, 1900, **33**, 3401), among others, showed that the perfume of anise is commonly associated with this group, and our own experiments with aromatic azoimides (Trans., 1907, **91**, 855, 1350, 1942) furnished several examples of odour-intensification by the group in question. This effect is not merely absent from the aliphatic derivatives, it is actually reversed. The faint odour of triazoacetic acid is not comparable with that of acetic acid itself, and the next higher homologue, although more markedly suggesting rancidity, is far inferior to propionic acid in pungency; the relationship of the esters is parallel, the powerful, characteristic fragrance of ethyl acetate being almost entirely suppressed by introducing the triazo-group, whilst the odour of triazoacetone is much more feeble than that of the unsubstituted ketone. Almost equally marked is the reversal of the azoimide character in respect of actinism. Aromatic triazo-derivatives are seldom obtainable free from colour, and the great majority rapidly darken when exposed to diffused light, but the aliphatic derivatives hitherto examined have been remarkably free from this peculiarity; specimens of ethyl triazoacetate, ethyl α- and β-triazopropionates, triazoacetamide, triazopropionamide, and of the free acids, have given no indication of discoloration by light.

A few days after the appearance of our previous paper (this vol., page 72), a description of triazoacetic ester was published by Curtius, Darapsky, and Bockmühl (*Ber.*, 1908, **41**, 344), who, having obtained the hydrazide of the acid by the action of hydrazine on diazoacetic ester, as also from diazoacetamide and hydrazine hydrate, proceeded to verify their diagnosis by the interaction of iodoacetic ester and silver azide; in reply to an inquiry, Geheimrat Professor Curtius has informed us that he will not regard the further prosecution of our investigation as an encroachment on his own researches, for which courtesy we beg to offer him our best thanks.

EXPERIMENTAL.

α-Triazopropionic Acid, $CH_3 \cdot CHN_3 \cdot CO_2H$.

Twenty grams of purified α-triazopropionic ester were mixed with absolute alcohol and shaken with potassium hydroxide (1 mol.) dissolved in 50 c.c. of water; the temperature rose, and the ester dissolved without liberation of gas or development of colour. After removing alcohol on the water-bath, slight excess of dilute sulphuric acid was added to the cold solution, and this having been extracted four times with ether, the solvent was dried with sodium sulphate and evaporated. The residual oil was then heated at 50° during a three hours' exposure to a pressure of 2 mm., but no attempt was made to distil the acid, since it appeared unsafe to heat any quantity of the material above 100°. Immersed in a freezing mixture of ice and salt, the acid became viscous, but did not solidify; nevertheless, on surrounding the substance with solid carbon dioxide, it froze to a tough, crystalline cake, and on raising the temperature very slowly the crystals melted at zero:

0·1744 gave 0·2030 CO_2 and 0·0723 H_2O. $C = 31·74$; $H = 4·62$.
0·1654 ,, 52·4 c.c. of nitrogen at 20° and 751 mm. $N = 36·47$.
$C_3H_5O_2N_3$ requires $C = 31·31$; $H = 4·35$; $N = 36·52$ per cent.

α-Triazopropionic acid has a rancid odour, more pronounced than that of triazoacetic acid; when thrown on a hot plate, it detonates with a moderate explosion and takes fire. Interaction with concentrated sulphuric acid is most violent, torrents of gas accompanied by white smoke being produced, whilst the residual liquid is very dark brown; this behaviour is quite distinct from that of triazoacetic acid, which the higher homologue resembles, however, in yielding nitrogen when mixed with stannous chloride in hydrochloric acid.

The Silver Salt.—On adding silver nitrate to a neutral solution of ammonium α-triazopropionate, a white, crystalline precipitate was formed, and, being moderately soluble in boiling water, was recrystallised therefrom, forming minute, lustrous needles:

0·3593 gave 0·1385 Ag. Ag = 48·48.

0·1276 „ 21·6 c.c. of nitrogen at 24° and 761 mm. N = 19·48.

$C_3H_4O_2N_3Ag$ requires Ag = 48·63; N = 18·93 per cent.

The substance detonates when heated, and is much more sensitive towards light than silver triazoacetate.

Action of Alkali.—An aqueous solution of the potassium salt is neutral, and may be evaporated without change, but if excess of alkali is present, effervescence takes place, and, on increasing the preponderance of potassium hydroxide, liberation of nitrogen and ammonia becomes torrential, and a deep yellow coloration is developed in the liquid, from which crystals subsequently separate. Several grams of the acid were therefore heated on the water-bath with excess of potassium hydroxide until ammonia was no longer liberated, and then acidified with dilute sulphuric acid, which gave no trace of hydrazoic acid; the deep yellow liquid was extracted ten times with ether, which, when dried, deposited a solid residue on evaporation. After trituration with a small quantity of cold water, the drained residue was crystallised from a mixture of ethyl acetate and petroleum, yielding indefinite crystals, which evolve gas at 153°, changing to a dark brown semi-solid. Analysis points to a condensation product of obscure composition, possibly, $C_{10}H_{11}O_6N$, but the amount of material at our disposal was too small to justify a definite pronouncement. The substance dissolves in alkalis, and is reprecipitated by acids; a neutral solution of the ammonium salt develops an intense, but dirty, violet coloration with ferric chloride, and silver nitrate gives a pale yellow, curdy precipitate in the same solution, becoming very dark brown in the course of a few seconds.

Ethyl α-Triazopropionate, $CH_3{\cdot}CHN_3{\cdot}CO_2{\cdot}C_2H_5$.

One hundred grams of ethyl α-bromopropionate, mixed with 50 grams of absolute alcohol, were heated under reflux during twenty hours with 50 grams of sodium azide dissolved in water. After steam distillation, crystallised sodium acetate was dissolved in the condensed liquid, from which the heavy ester was removed mechanically in almost quantitative yield. The product was shaken twice with water, dried with calcium chloride, and distilled under 2 mm. pressure, when it boiled very steadily to the last few drops at 46°:

0·1881 gave 0·2929 CO_2 and 0·1113 H_2O. C = 42·47 ; H = 6·61.
$C_5H_9O_2N_3$ requires C = 41·96 ; H = 6·29 per cent.

The difficulties experienced in attempting to estimate nitrogen in triazoacetic ester were reproduced by the present ethereal salt, and the ordinary method of combustion gave two results indicating 4 per cent. in excess of the theoretical amount. We are indebted to Mr. H. Droop Richmond, however, for estimations of nitrogen by the following process, devised by him, and which he is describing elsewhere. A weighed quantity of the ester, with two drops of formaldehyde solution, was washed into a nitrometer with 0·5 c.c. of alcohol, and, 10 c.c. of concentrated sulphuric acid having been introduced, the volume of gas was measured. The liquid was washed into a flask with 5 + 3 + 2 c.c. of concentrated sulphuric acid, 2 grams of zinc dust and one drop of mercury were added, and the product boiled until colourless; on addition of alkali and alkali sulphide, followed by distillation, the ammonia was collected:

0·1400 gave 22·9 c.c. of nitrogen at 18° and 752 mm., along with 0·0176 of ammonia. N = 18·99 as gas, 10·36 as NH_3 ; total 29·35.
$C_5H_9O_2N_3$ requires N = 29·37 per cent.

Incidentally, Mr. Richmond's experiments have brought to light a curious point in connexion with the action of sulphuric acid on the triazo-esters. In describing triazoacetic ester, we referred to the abnormal action of the concentrated acid, which liberated almost exactly one-half the nitrogen, instead of two-thirds; Mr. Richmond finds, however, that the amount set free approximates closely to two-thirds if the ester is first mixed with alcohol.

α-Triazopropionic ester is a colourless, limpid oil, with a perfume more pronounced than that of triazoacetic ester, and faintly suggesting ethyl acetoacetate; it is readily volatile in steam, the vapour producing a throbbing sensation when inhaled. The specific gravity is 1·065 at 23° compared with water at the same temperature. On mixing the substance with concentrated sulphuric acid, gas evolution is immediate and vigorous, taking place much more readily than in the case of ethyl triazoacetate; with stannous chloride in hydrochloric acid, however, action is more sluggish, although ultimately becoming quite brisk. When thrown on a hot plate, the ester takes fire without detonation.

α-*Triazopropionamide*, $CH_3\cdot CHN_3\cdot CO\cdot NH_2$.

α-Triazopropionic ester, mixed with alcohol, was shaken with aqueous ammonia until the emulsion disappeared, when the residue left by evaporation rapidly solidified on cooling; the drained product was recrystallised from hot benzene, which dissolves it freely, depositing lustrous, transparent, rectangular plates, melting at 79°:

0·1661 gave 68·7 c.c. of nitrogen at 19° and 780 mm. N = 49·65.
$C_3H_6ON_4$ requires N = 49·12 per cent.

When thrown on a hot plate, the amide vaporises without ignition or detonation. A solution in concentrated sulphuric acid effervesces feebly when stirred, but the substance is attacked immediately by a cold 40 per cent. solution of potassium hydroxide, evolution of nitrogen and ammonia becoming very vigorous on heating, when the liquid develops a yellow colour; the volume of nitrogen remaining after the ammonia is absorbed falls far short of the 24·5 per cent. to be expected if the triazo-group underwent the change first noticed in the case of camphorylazoimide.

A hot aqueous solution of α-triazopropionamide dissolves yellow mercuric oxide, and the product yields with hydroxylamine hydrochloride a transient yellow precipitate which quickly becomes colourless.

Ethyl β-Triazopropionate, $N_3·CH_2·CH_2·CO_2·C_2H_5$.

Seventy grams of ethyl β-iodopropionate, mixed with alcohol, were heated with 30 grams of sodium azide in the minimum of water during six hours under reflux. The action proceeds slowly, and is complicated if the liquid is boiled; moreover, it appears to be reversible, and only by separating the product and heating it twice again with sodium azide was the triazopropionate obtained quite free from iodine. In this way there were prepared about 15 grams of ester boiling at 62° under 5 mm. pressure, but, although a test for iodine gave a negative result, the estimation of nitrogen, both by the ordinary method and by Richmond's process, gave low results:

0·1168 gave 28·85 c.c. of nitrogen at 16° and 751 mm. N = 28·83.
$C_5H_9O_2N_3$ requires N = 29·37 per cent.

β-Triazopropionic ester is colourless and limped, with an odour fainter than that of the α-compound, whilst the specific gravity is greater, being 1·087 at 19° compared with water at the same temperature, and the same relationship is observed in the case of the α- and β-chloropropionic esters; it is readily volatile in steam, when the vapour produces the characteristic throbbing sensation if inhaled. On a hot plate, the ester takes fire without detonation.

Action of Alkali.—In marked distinction from ethyl α-triazopropionate, the β-ester cannot be hydrolysed without removing the triazo-group; an unsuccessful attempt was made to prepare the amide by shaking the ester with aqueous ammonia, but even this eliminates hydrazoic acid. On heating the ester with alcoholic potassium hydroxide, the effervescence which characterises those compounds in which the triazo-group occupies the α-position in relation to carbonyl is suppressed, and the products are hydrazoic and acrylic acids.

3-*Triazobutanone*-2, $CH_3 \cdot CO \cdot CHN_3 \cdot CH_3$.

The isomeric chloro-derivatives of methyl ethyl ketone required for the production of the corresponding azoimides were prepared in the manner described by Kling (*Compt. rend.*, 1905, **140**, 312), but, on finding that the proportion of chlorine could be largely increased without perceptible formation of dichloro-derivatives, we used 250 grams of marble for 500 grams of methyl ethyl ketone; 100 c.c. of water were present at the outset, and 400 c.c. were added in quantities of 50 c.c. at intervals of one hour, the temperature of chlorination being 40—60°. The product having been dried with sodium sulphate, unchanged ketone was removed by fractionating under 760 mm. pressure with a column of the rod-and-disk pattern, the separation of the chloro-ketones being best conducted under reduced pressure. The yield of 3-chlorobutanone-2 from the above quantity of methyl ethyl ketone reached 220 grams, only 70 grams of 1-chlorobutanone-2 being obtained in satisfactory condition after five fractionations; under 40 mm. pressure, the substances boiled at 46° and 63° respectively.

Sixty grams of 3-chlorobutanone-2 were shaken with an aqueous solution of sodium azide containing 40 grams, rendered faintly acid with acetic acid; after twenty-four hours, the heavy oil was extracted with ether, dried by sodium sulphate, and distilled under 2 mm. pressure, the yield being nearly quantitative. The product was again shaken with the desiccating agent and redistilled, boiling at 46° under 2 mm. pressure, and having specific gravity 1·057 compared with water at 18°:

0·0925 gave 28·4 c.c. of nitrogen at 13° and 771 mm. $N = 37 \cdot 17$.

$C_4H_7ON_3$ requires $N = 37 \cdot 17$ per cent.

The triazobutanone is a colourless, refractive liquid, with a sour, vinous odour, much less irritating than that of the chloro-compound; it mixes with organic media, is moderately soluble in water, and is readily volatile in steam. The freshly-prepared substance is more stable than triazoacetone, and may be kept in darkness during two weeks without undergoing change of appearance; ultimately, however, it becomes yellow, this alteration being accelerated by exposure to light. When dropped on a hot plate, it vaporises without ignition or detonation. Concentrated sulphuric acid decomposes the azoimide immediately, as in the case of triazoacetone, vigorous effervescence taking place; phenylhydrazine also has marked action, but has not led to a definite compound.

Action of Alkali.—The behaviour of 3-triazobutanone-2 towards aqueous alkalis recalls that of acetonylazoimide. The concentrated agent gives rise to vigorous liberation of gas, with development of a red coloration; more dilute alkali (2 per cent.) furnished the nitrogen at a rate convenient for measurement:

0·2488 gave 43·0 c.c. of nitrogen at 18° and 775 mm. N = 20·7.
$C_4H_7ON_3$ requires 2/3 N = 24·8 per cent.

On decomposing a larger quantity of material, it was easy to show that the above deficit of nitrogen was due to elimination of hydrazoic acid, and the presence of an oxidisable product is indicated by the action of Fehling's solution. It is noteworthy that the first action of the alkali appears to be dissolution, because, on mixing the triazo-ketone cautiously with a deficit of very dilute potassium hydroxide, a pale yellow solution has been obtained which is found to contain the azoimide even after repeated extraction with ether; although the presence of the triazo-group in this solution is demonstrated by vigorous effervescence with concentrated alkali, an attempt to prepare a benzoyl derivative of the hypothetical enolic modification was unsuccessful.

The Semicarbazone.—On mixing the triazo-ketone with aqueous semicarbazide hydrochloride in molecular proportion and adding sodium acetate, the semicarbazone was precipitated as a paste from which a disappointing yield of crystallised material was obtained; this unsatisfactory result must be due to subsidiary changes, because free hydrazoic acid was recognisable. On recrystallising the drained product from boiling water, followed by a mixture of benzene and petroleum, lustrous, snow-white plates were obtained, melting at 94° without apparent decomposition:

0·0810 gave 34·0 c.c. of nitrogen at 16° and 771 mm. N = 50·25.
$C_5H_{10}ON_6$ requires N = 49·41 per cent.

The semicarbazone is a stable substance, easily soluble in common media, excepting petroleum, and moderately soluble in cold water. Concentrated alkali sets free nitrogen and eliminates hydrazoic acid, whilst concentrated sulphuric acid decomposes it almost explosively, provided the crystals are in proper contact with the agent from the outset. When the triazo-ketone remains associated with semicarbazide during several days, there is produced a sparingly soluble substance which is probably the bis-semicarbazone of dimethylglyoxal (compare this vol., page 83).

Action of Hydroxylamine.—Owing to the readiness with which hydrazoic acid is eliminated from 3-triazobutanone-2, we have failed in attempts to prepare an oxime. On applying to this ketone the process which led to triazoacetoxime, oximation took place very readily, but hydrazoic acid was eliminated, and the liquid product, although containing a large proportion of the required oxime, gave a quantity of nitrogen almost 5 per cent. below the calculated amount;

moreover, the colourless substance became dark yellow during twelve hours, spontaneously liberating hydrazoic acid. Nevertheless, the behaviour of triazoacetoxime led us to try the action of *p*-toluenesulphonyl chloride, in the hope that a definite derivative might be obtainable; the experiment, however, was unsuccessful, as, although conducted in exactly the same way as in the case of triazoacetoxime and of 1-triazobutanonoxime-2 (see below), the oily product, even in dilute ethereal solution, spontaneously liberated hydrazoic acid and did not yield a crystalline derivative.

On treating the triazo-ketone with excess of hydroxylamine hydrochloride, a small proportion of dimethylglyoxime was obtained, easily recognised by the brilliant red, crystalline precipitate which separated on adding nickel sulphate followed by ammonia.

1-*Triazobutanone*-2, $N_3 \cdot CH_2 \cdot CO \cdot CH_2 \cdot CH_3$.

Seventy grams of the chlorobutanone were shaken with fifty grams of sodium azide dissolved in 300 c.c. of water containing a few drops of acetic acid, the intensely pungent odour of the halogen derivative being no longer perceptible after six or eight hours. The oil was then extracted with ether, dried by sodium sulphate, and distilled under 2 mm. pressure, the major portion boiling at 56°, and having specific gravity 1·084 compared with water at 18°:

0·1102 gave 34·4 c.c. of nitrogen at 16° and 779 mm. N = 37·82.

$C_4H_7ON_3$ requires N = 37·17 per cent.

In appearance, volatility, and behaviour towards solvents, the "external" azoimide is indistinguishable from the "internal" derivative, but the odour is faint and without character. Although immediately attacked by concentrated sulphuric acid, the substance is more stable than the isomeride towards light, becoming only faintly yellow in the course of several weeks. Thrown on a hot plate, it takes fire with a feeble detonation, thus presenting a curious distinction from the "internal" azoimide.

Action of Alkali.—Qualitatively, there is no difference between the two isomerides in regard to their behaviour towards alkali, but, on measuring the nitrogen evolved, it appeared that 1-triazobutanone-2 yields a slighty larger proportion in the elemental form:

0·1731 gave 32·0 c.c. of nitrogen at 18° and 781 mm. N = 22·3.

$C_4H_7ON_3$ requires 2/3 N = 24·8 per cent.

The deficit from the calculated amount is due to elimination of hydrazoic acid.

The Semicarbazone.—The superior stability of the "external" azoimide is indicated also by its behaviour towards semicarbazide; this gave a quantitative yield of the semicarbazone, which was recrystallised from boiling water followed by hot benzene, the latter solvent depositing lustrous, felted, snow-white needles melting at 101°:

0·1292 gave 53·2 c.c. of nitrogen at 18° and 779 mm. N = 49·51.
$C_5H_{10}ON_6$ requires N = 49·41 per cent.

The compound dissolves less readily than the isomeride in benzene and in water, but its behaviour towards alkali, Fehling's solution, and sulphuric acid is that of the "internal" triazo-derivative; a mixture of the two substances melted at 70—75°, and the individuals behave alike on a hot-iron plate, merely charring without detonation.

Triazomethyl Ethyl Ketoxime, $N_3 \cdot CH_2 \cdot C(:NOH) \cdot C_2H_5$.

Ten grams of 1-triazobutanone-2 were shaken with an aqueous solution of hydroxylamine, prepared from 7 grams of the hydrochloride and 5 grams of sodium carbonate; oximation proceeded rapidly, and the product, after extraction with ether, was dried during two days in a vacuum desiccator containing sulphuric acid:

0·1150 gave 42·5 c.c. of nitrogen at 21° and 776 mm. N = 43·81.
$C_4H_8ON_4$ requires N = 43·75 per cent.

The odour of the oxime resembles that of the free ketone, but is much fainter. Dilute aqueous potassium hydroxide dissolves the substance without effervescence, but, on warming the solution, nitrogen is liberated, whilst the liquid reduces Fehling's solution immediately and yields hydrazoic acid when acidified.

The p-*Toluenesulphonyl Derivative.*—The oxime, dissolved in pyridine, was mixed with the calculated quantity of *p*-toluenesulphonyl chloride in the same solvent, but the oil which separated on dilution with water furnished a very unsatisfactory yield of the toluenesulphonyl derivative. Recrystallisation from petroleum gave lustrous, colourless needles melting at 72°, when liberation of gas took place, followed by an explosion:

0·1827 gave 31·2 c.c. of nitrogen at 20° and 776 mm. N = 20·32.
$C_{11}H_{14}O_3N_4S$ requires N = 19·86 per cent.

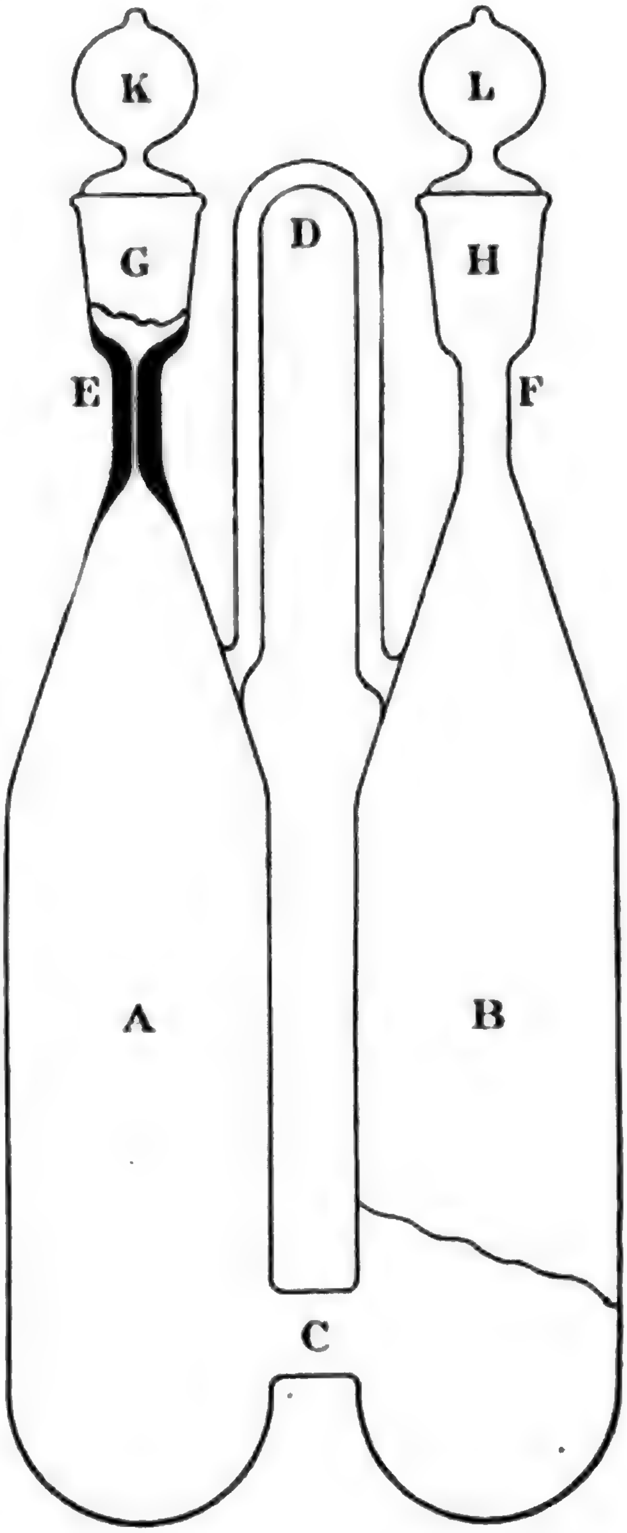
The substance yields nitrogen with alkali and with sulphuric acid; although snow-white when freshly prepared, it rapidly deteriorates, and becomes brown in a few days even when protected from light.

ROYAL COLLEGE OF SCIENCE, LONDON,
SOUTH KENSINGTON, S.W.

LXII.—*A New Form of Pyknometer.*

By WILLIAM ROBERT BOUSFIELD, M.A., K.C.

THE volume which a solute occupies in a solution is now recognised as giving a most valuable insight into the nature of the solution. The contraction which takes place on solution in water is probably in many cases the best basis for the estimation of the amount of water combination which accompanies the process of solution. Moreover, very exact quantitative relations often exist between the variations of such contraction for a series of dilutions and the corresponding variations of other physical properties of the solution.* For the accurate determination of solution volumes in dilute solutions, it is necessary to have density determinations which are relatively accurate within a unit in the fifth place of decimals, and it is desirable to be able to attain such degree of accuracy with an ease of manipulation which does not evolve troublesome precautions. It is with the object of meeting these requirements, that the present form of pyknometer has been designed.



It consists of two tubes, *A* and *B*, connected as shown by a short tube, *C*, and by a handle, *D*, which serves to suspend the apparatus at a suitable height in a thermostat. The tubes *A* and *B* are conical at their upper ends, and are joined by tubes *E* and *F* of fine bore to conical cups *G* and *H*, which can be closed by stoppers *K* and *L*.

---

* See Bousfield on "Ionic Size in Relation to the Physical Properties of Aqueous Solutions," *Phil. Trans.*, 1906, *A*, 206, 146, 150.

To fill the pyknometer, the stoppers *K* and *L* are replaced by stoppers furnished with suitably bent tubes, one of which is inserted into the vessel containing the liquid with which the pyknometer is to be filled, whilst the other tube may be conveniently connected to a filter pump or other exhauster. The filling operation is completed by pouring a little of the liquid into one of the cups, and sucking air from the other.

The cups are usually left partly filled with liquid until the temperature adjustment is attained. The excess of liquid is then sucked out, and the last portions removed by a piece of filter paper screwed to a fine point. The level is adjusted to marks on the tubes *E* and *F*, which are made just where the cups narrow down to the size of the fine bore. Before removal from the thermostat, the cups are wiped dry with a suitable swab and the stoppers inserted. The apparatus combines the following advantages.

1. It serves for determinations at temperatures either above or below the temperature of weighing, and the cups, which hold the overflow when the liquid expands before weighing, can be wiped dry so as not to run the risk of vitiating the observation by adherent moisture.

2. The apparatus acts as a very sensitive thermometer when the level of the liquid has been adjusted. It can then be left a minute or two longer in the thermostat, and an observation of the level with a magnifying lens indicates at once whether the temperature of the thermostat has been attained.

3. The reduction of pressure in the operation of filling tends to extract some of the air dissolved in the liquid and to reduce the formation of bubbles. Any air bubbles that are present at any stage can be detached by shaking or inverting the pyknometer, and can be readily expelled by sucking some of the liquid into the cup on one side or the other.

4. The pyknometer, although light, is so strong that it will bear some amount of rough handling, and, in particular, it can be wiped dry with some vigour, after taking from the thermostat, without risk of breakage.

As an example of the degree of accuracy of which the apparatus is capable in ordinary use, there is appended a set of densities of nitric acid of normal strength taken with two pyknometers both constructed as above described, the total content of pyknometer No. 1 being about 250 c.c. and of pyknometer No. 2 about 350 c.c.:

Densities of Normal Nitric Acid.

Temp.	Densities. Pyk. No. 1.	Densities. Pyk. No. 2.	Difference.
4°	1·035801	1·035796	5
11	1·034336	1·034341	–5
18	1·032435	1·032442	–7
25	1·030159	1·030167	–8

The weighings were taken with only ordinary precautions as to observation of temperature and barometric pressure. The maximum difference in the results from the two pyknometers is less than ± 1 in the fifth place of decimals.

LXIII.—*Para- and Meta-nitrosoacetanilide.*

By John Cannell Cain.

The discovery by Piloty, in 1898 (*Ber.*, **31**, 456), that nitroso-compounds can exist in two modifications, namely, a solid, colourless, bimolecular and a liquid, blue, unimolecular, has been confirmed by the observations of several investigators. It is found that the colourless, bimolecular form melts to a blue liquid consisting of the unimolecular modification, and also becomes dissociated in certain solvents, the solutions being blue or green.

In the course of the present investigation, carried out with the object of preparing *p*-nitrosoacetanilide, which, unlike many analogous compounds, cannot be obtained from *N*-nitrosoacetanilide by intramolecular change (compare O. Fischer and Hepp, *Ber.*, 1887, **20**, 2474), the interesting fact was discovered that, whilst the compound can be prepared in both the unimolecular and the bimolecular state, both these modifications are well-defined solids. So far as the author is aware, this phenomenon has not been previously observed.

The unimolecular *p*-nitrosoacetanilide is obtained from alcohol in large, green crystals melting with decomposition at 173°, and the bimolecular variety separates from water as a white, microcrystalline powder melting without decomposition at 180—181°.

In the case of *m*-nitrosoacetanilide, which was also prepared, the solid, green, unimolecular modification is transformed in solution so readily into the bimolecular form that it could not be isolated in the pure condition. The bimolecular variety is yellowish-brown, and yields green solutions in water, alcohol, or acetic acid.

The method of preparation of these nitroso-derivatives was the same as that employed by Leuchs (*Ber.*, 1907, **40**, 1086) for *o*-nitrosoacetanilide, namely, by oxidising the corresponding monoacetylphenylenediamine with Caro's acid. The occurrence of a bimolecular modification of the ortho-compound was not recorded by Leuchs or by Brand and Stohr (*Ber.*, 1906, **39**, 4085), who first prepared the substance by another method.

EXPERIMENTAL.

p-*Nitrosoacetanilide.*

Concentrated sulphuric acid (64 grams) was stirred into potassium persulphate (32 grams), and the mixture allowed to remain at the ordinary temperature for one hour. It was then poured on ice, exactly neutralised with potassium carbonate (about 105 grams), and a few drops of acetic acid added. The volume of the ice-cold solution was about 1—1½ litres, and it contained 1·07 grams of active oxygen.

On pouring this solution into a cold solution of 5 grams of monoacetyl-*p*-phenylenediamine in about 400 c.c. of water, a greenish-grey, flocculent precipitate was formed. This was collected, extracted with ether, and the grey solid, left after evaporation of the ether, was crystallised from alcohol. On cooling, *p*-nitrosoacetanilide (about 1 gram) separated in stout, green plates, melting at 173° with decomposition:

0·1208 gave 18 c.c. of nitrogen at 18° and 748 mm. N = 17·24.

$C_8H_8O_2N_2$ requires N = 17·10 per cent.

p-*Nitrosoacetanilide* gives Liebermann's reaction, and is readily soluble in alcohol or glacial acetic acid, very sparingly so in water, and insoluble in benzene. It dissolves in aqueous caustic alkalis with a yellow colour, and the solution, on heating, evolves ammonia.

In one experiment, in which the oxidation of the same weight of monoacetyl-*p*-phenylenediamine was carried out by using less potassium persulphate (26·3 grams), in addition to *p*-nitrosoacetanilide there was also isolated a substance insoluble in ether, but soluble with a red colour in alcohol, separating from the latter in yellow needles, which proved to be 4:4′-diacetyldiaminoazobenzene (Mixter, *Amer. Chem. J.*, 1883, **5**, 282). In an experiment, using excess of persulphate (40 grams), a small quantity of *p*-nitroacetanilide was detected.

bis-p-*Nitrosoacetanilide.*

On adding water to the alcoholic mother liquors from *p*-nitrosoacetanilide, nearly colourless crystals were obtained, which were quite different in habit from the first crop. On recrystallisation from hot water, these separated in the colourless condition, but they gradually acquired a pale green tinge when dried between filter paper. The substance melts at 180—181° without decomposition, gives Liebermann's reaction, and evolves ammonia on heating with aqueous potassium hydroxide:

0·1359 gave 19·6 c.c. of nitrogen at 18° and 768 mm. N = 17·18.
$C_{16}H_{16}O_4N_4$ requires N = 17·10 per cent.

bis-p-*Nitrosoacetanilide* is readily soluble in alcohol or glacial acetic acid, and moderately so in hot water, being much more soluble in the latter solvent than is the unimolecular compound; it is insoluble in benzene. Its formation from *p*-nitrosoacetanilide is readily demonstrated by boiling the latter with a little water in a test-tube, when, on cooling, a white, microcrystalline powder of the bimolecular compound collects above the excess of the green, unimolecular modification.

As was to be expected from the green colour of the solution in glacial acetic acid, the substance was found, by a cryoscopic determination of the molecular weight, to be dissociated in this solvent.

bis-m-*Nitrosoacetanilide*.

This was obtained from monoacetyl-*m*-phenylenediamine in exactly the same way as described for the para-derivative. The base was prepared by acetylating *m*-phenylenediamine. Instead, however, of isolating the free base, the hydrochloride was crystallised from hot water, the dry substance dissolved, neutralised with potassium hydroxide, filtered, and the filtrate titrated with *N*/2-sodium nitrite. For the oxidation, the requisite amount of the solution was used. On mixing this solution with the Caro's acid, a yellowish-brown coloration was observed. The ethereal extract was green, and when moderately dilute left a residue partly green and partly yellowish-brown, the former evidently consisting of the unimolecular modification of the nitroso-compound. When, however, more concentrated ethereal solutions were allowed to stand, the bimolecular variety was gradually formed and crystallised out. Hence it was not found practicable to isolate the unimolecular form in the pure state.

On crystallisation from alcohol, pale yellowish-brown, microcrystalline needles, melting at 111°, separated on cooling. The colour was not changed by repeated crystallisation. From analogy to the numerous examples in the literature, there can be little doubt that these consisted of the bimolecular form. As, however, the substance is insoluble in the ordinary indifferent solvents, the molecular weight in such solvent could not be determined. An estimation in glacial acetic acid showed that the substance was completely dissociated to the unimolecular form in this solvent:

0·097 gave 14·5 c.c. of nitrogen at 16·5° and 742 mm. N = 17·29.
$C_{16}H_{16}O_4N_4$ requires N = 17·10 per cent.

bis-m-*Nitrosoacetanilide* gives Liebermann's reaction, is readily soluble in alcohol, glacial acetic acid, acetone, or hot water, with a green colour, but insoluble in ether, benzene, or light petroleum. The substance does not dissolve in caustic alkalis, and, on heating, no ammonia could be detected.

Sir William Ramsay's kindness in allowing me to carry out this work at University College is here gratefully acknowledged.

UNIVERSITY COLLEGE,
LONDON.

LXIV.—*The Constitution of "Thiocyanates" containing an Electronegative Group.*

By AUGUSTUS E. DIXON and JOHN TAYLOR.

So long ago as 1884, Gebhardt noticed (*Ber.*, **17**, 2088) the ease with which certain trisubstituted thiocarbamides are dissociated into thiocarbimide and secondary amine, a change induced even by distillation in a current of steam. Curiously enough, heat seems to be somewhat variable in its effect, for whilst *ab*-diphenyl-*a*-methylthiocarbamide by dry distillation is resolved into its constituents, namely, phenylthiocarbimide and methylaniline, yet, on the other hand, if these are boiled together under a reflux apparatus, they unite to form the trisubstituted thiocarbamide.

As a rule, no difficulty was encountered in producing the thiocarbamides, compounds being obtained of phenylthiocarbimide with methyl- or ethyl-aniline, of *p*-tolylthiocarbimide with the same two amines, and of *a*-naphthylthiocarbimide with methylaniline.

Diphenylamine, however, proved an exception; thus, it failed to unite with phenylthiocarbimide either directly or when the two substances were heated together for a whole day in boiling cumene at 165°. Nevertheless, when they were heated for several days in a sealed tube at 280°, the product, a dark red oil, yielded traces of a yellow, crystalline material, which, after purification, melted at 152°, and was identified as triphenylthiocarbamide. Further, Gebhardt could not obtain from diphenylamine, by means of potassium cyanate or thiocyanate, the corresponding urea or thiocarbamide; Miquel, too, has placed on record the failure of an attempt to combine this base with benzoylthiocarbimide (*Ann. Chim. Phys.*, 1877, [v], **11**, 346).

Subsequently, E. A. Werner mentioned in a brief note (Proc., 1892, **8**, 96) that *aa*-diphenylthiocarbamide may be obtained through the isomeric rearrangement of diphenylamine thiocyanate.

Since Gebhardt's paper was published, no further attempt seems to have been made to combine diphenylamine with thiocarbimides; perhaps because his results did not seem very encouraging.

It occurred to us, however, that the acyl "thiocyanates" or "thiocarbimides," being very active substances, might possibly be able to unite with this rather inert base, and, on putting the conjecture to the test of experiment, we found that combination occurs very readily, and often with the development of much heat. These reactions furnish the means of obtaining a new series of substituted thiocarbamides, isomeric with the known forms having two aryl radicles symmetrically distributed between the two nitrogen atoms, that is, the substituted thiocarbanilides and their strict congeners. For the purpose of comparison, and to test the generality of the reaction, we have now prepared several members of the *aa*-diphenylated class, which are described later.

Concurrently with these syntheses, we have taken the opportunity to prepare, in a more or less pure condition, certain acyl "thiocarbimides," and have determined for these substances some of the physical constants and chemical properties which appear to bear upon the subject of their chemical constitution.

Boiling points were taken by means of short Anschütz thermometers, divided into fifths of a degree, the thread of mercury being totally immersed in the vapour; densities, either by a Westphal balance with 5 c.c. plummet, or by a Sprengel's pyknometer, containing about 7·5 c.c.; the indices of refraction were measured by means of a Pulfrich total-reflectometer, reading directly to 0·5° of arc, and by vernier to single minutes. Sodium light was employed, the molecular refractions, M_D, being calculated from the formula

$$M_D = \frac{(\mu_D - 1)p}{d\frac{t^\circ}{4^\circ}},$$

where μ_D = refractive index for the *D*-line at t°, p = molecular weight, and $d\frac{t^\circ}{4^\circ}$ = specific gravity at the observed temperature t°, referred to water at 4°. Where atomic refractions are used for the purpose of calculation, the values are taken as follows:

$$C = 5{\cdot}1;\ H = 1{\cdot}3;\ O\!: = 3{\cdot}4;\ \cdot O \cdot = 3{\cdot}1.$$

Acetyl Thiocyanate.

When Miquel first obtained (*loc. cit.*, 295) from acetyl chloride and lead thiocyanate a substance, $CH_3\cdot CO(CNS)$, he judged from the fact of its yielding with water, acetic and thiocyanic acids, but little carbonyl sulphide, that it must necessarily be acetyl thiocyanate, $CH_3\cdot CO\cdot SCN$, a view consistent, moreover, with its mode of formation. But the corresponding benzoyl compound, which combined with ammonia, aniline, and so on, to form substituted thiocarbamides, and which, on treatment with hot water, rapidly gave carbonyl sulphide, but no material amount of thiocyanic acid, he naturally classed as a thiocarbimide. Consequently, on finding that acetyl thiocyanate yielded with ammonia nothing that could certainly be recognised as acetylthiocarbamide, but, on the other hand, gave acetylphenylthiocarbamide when mixed with aniline, he felt compelled to regard the latter reaction as "abnormal."

Many homologues of acetyl thiocyanate have since been obtained by a similar method, and shown to possess the same abnormal or thiocarbimidic properties, especially when treated with particular materials or under particular conditions.

If that behaviour of acetyl "thiocyanate" which results in the separation of its constituents into $CH_3\cdot CO\cdot$ and $\cdot SCN$ be considered "thiocyanic," its direct union with alcohols, amines, &c., being regarded as "thiocarbimidic," acetyl thiocyanate acts normally both as such and as a thiocarbimide. For instance, it has been shown by Dixon and Hawthorne (Trans., 1905, **87**, 468) that when aniline acts on acetyl thiocyanate, the product at high temperatures consists mainly of acetylphenylthiocarbamide, whilst at low temperatures little is formed save aniline thiocyanate together with acetanilide; at intermediate temperatures both processes run concurrently, the distribution of the sulphur into thiocyanate and thiocarbamide becoming equal in the neighbourhood of 80°. Further, it was shown that if previously to interaction at a given temperature the thiocyanate was heated to a higher point and then cooled, the result as regards distribution of the sulphur was the same as if the preliminary heating had been omitted; so that if heating conditioned change of the thiocyanate into the isomeric thiocarbimide, such change must be temporary only, that is, reversible with alteration of temperature.

Following up these observations, Hawthorne (Trans., 1906, **89**, 536) obtained acetyl thiocyanate in a highly purified condition, and, having verified that it possesses a constant boiling point, ascertained that the molecular refractive power undergoes no change when the substance is examined at widely varying temperatures, from which it follows that isomeric change of the CNS group does not occur in these circumstances. Moreover, he found that the molecular refractive power of this group, whilst diverging considerably from that measured for certain known thiocyanates, agreed closely with the value determined experimentally for a number of undoubted thiocarbimides; hence he concluded that, so far as this static method may be relied on, acetyl "thiocyanate" is really a thiocarbimide, $CH_3{\cdot}CO{\cdot}NCS$.

Propionylthiocarbimide gave with aniline results very similar to those with acetylthiocarbimide, but, when the latter was combined with *o*-toluidine, the percentage of sulphur forming acetyl-*o*-tolylthiocarbamide was much higher than with aniline.

It may fairly be concluded from these results, that the thiocyanic or thiocarbimidic power of acetyl "rhodanide" is not inherent in the molecule, but is determined by external factors. Whatever the constitution of acetyl rhodanide may be, whether thiocyanate or thiocarbimide, the substance, notwithstanding the apparent vagaries in its chemical behaviour, in respect of physical properties is plainly a definite compound. Since a thiocyanate could not give the additive compounds yielded by this substance and by its strict congeners, we consider that they must henceforth be regarded as thiocarbimides. That this view does not conflict with the production, in many reactions, of thiocyanic acid, we propose to establish by showing that, under suitable treatment, various other acyl thiocarbimides, compounds the thiocarbimidic behaviour of which is so clearly marked that no doubt is entertained regarding their constitution, may be caused in like manner to decompose with production of thiocyanic acid.

The statement, made above, that acetyl thiocyanate could not give certain additive compounds requires explanation. Acetylthiocarbamide is formed, according to Nencki (*Ber.*, 1873, **6**, 599), from thioacetic acid and cyanamide; here, the acetyl group, combined initially with sulphur, is found ultimately attached to nitrogen:

$$CH_3{\cdot}CO{\cdot}SH + CN{\cdot}NH_2 = CH_3{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH_2.$$

In this case, probably the compound $CH_3{\cdot}CO{\cdot}S{\cdot}C(\colon NH){\cdot}NH_2$ is first formed, the acetyl group then migrating, either directly or in exchange for hydrogen, to a nitrogen atom. Such movement of the acyl group from sulphur to nitrogen has now been observed in many cases (see, for example, Dixon and Hawthorne, Trans., 1907, **91**, 122; Dixon and Taylor, *ibid.*, 912; 1908, **93**, 18), so that with ammonia the action might be conceived to run thus:

$$Ac{\cdot}SCN + NH_3 = AcS{\cdot}C(\colon NH){\cdot}NH_2 \longrightarrow HS{\cdot}C(\colon NAc){\cdot}NH_2 \longrightarrow AcNH{\cdot}CS{\cdot}NH_2.$$

But in the case of union with aniline, if

$$Ac{\cdot}SCN + PhNH_2 = AcS{\cdot}C(\colon NH){\cdot}NHPh$$

and the acetyl group now migrates, yielding the actual product, namely, AcNH·CS·NHPh, it is not easy to understand why this group should pass, at very moderate temperatures, to the non-phenylated nitrogen atom, seeing that when the compound

AcS·C(:NH)·NHPh

is liberated from the corresponding hydrochloride (Dixon and Hawthorne, *loc. cit.*) the acetyl group goes to the other nitrogen, yielding AcPhN·CS·NH_2, a compound sufficiently stable to be recrystallised from boiling alcohol without undergoing change to the symmetrical form. But in any case it is unnecessary to labour this point, since the following observations are inconsistent with the view that acetyl rhodanide is a true thiocyanate.

Pure acetylthiocarbimide, when boiled with dilute caustic alkali, dissolved rapidly, with evolution of ammonia and production of alkali carbonate; one portion of the resultant clear liquid, when acidified and treated with ferric chloride, gave the reaction for thiocyanic acid; the other gave with lead acetate a copious precipitate of lead sulphide. But solution of lead thiocyanate in caustic alkali did not darken when boiled, nor was ammonia evolved; neither did pure sodium thiocyanate, when boiled with alkaline lead tartrate, yield these reactions; even ammonium thiocyanate (which might conceivably have changed to thiourea) suffered no desulphurisation under this treatment.

It is not easy to understand how true acetyl thiocyanate, if decomposed into acetic and thiocyanic acids, could have afforded the results described. But if acetylthiocarbimide is undergoing hydrolysis, a portion may escape the dissociation into acetyl and ·NCS, undergoing instead the usual thiocarbimidic change into carbonyl sulphide (which would account for the desulphurisation) and the amido-compound, acetamide, the further hydrolysis of which would yield ammonia.

Wheeler and Merriam, on the other hand, consider that the production of metallic sulphide by the action of boiling caustic alkali on a rhodanide cannot be regarded as evidence of its having a thiocarbimidic constitution, giving in support of this view the fact that benzyl thiocyanate gives the reaction mentioned (*J. Amer. Chem. Soc.*, 1901, **23**, 285). Benzyl thiocyanate, however, is somewhat readily transformable by heat into the isomeric thiocarbimide, which may possibly be the reason for the phenomenon.

There are, in fact, no decisive reasons for supposing any of the acyl rhodanides to be thiocyanates. In certain circumstances, no doubt, their decomposition products contain free or combined thiocyanic acid, but, as this property is not generally manifested by organic thiocyanates, its display by certain acyl derivatives can scarcely serve to correlate them with that class of compounds. Secondly, it is reasonable to suppose that highly electronegative radicles have but a feeble hold on the CNS group; hence, if these two become separated, and H·NCS cannot exist as such, the rhodanic group, unless decomposed, must necessarily be found as H·SCN, no matter how it was attached originally. That the union of R·CO· with nitrogen is much more easily broken than that of $R·CH_2·$ is shown by the different behaviour with alkali of $CH_3·CH_2·NH_2$ and of $CH_3·CO·NH_2$, the latter being readily hydrolysed into acetic acid and ammonia. If now the group CS be substituted for the hydrogen of the NH_2 group, the products being $CH_3·CH_2·NCS$ and $CH_3·CO·NCS$ respectively, it might be anticipated that these two would present some corresponding difference in their resistance to hydrolysis.

In the third place, amongst acyl rhodanides, this "thiocyanic" behaviour is rarely, if ever, displayed to the exclusion of "thiocarbimidic."* Thus, with acetyl rhodanide and *o*-toluidine, the yield of disubstituted thiocarbamide even at 12° was nearly 74 per cent. of the theoretical for a thiocarbimide, and at 85° reached more than 96 per cent. (Hawthorne, *loc. cit.*). With the homologues it is the same; thus, propionyl and *iso*butyryl rhodanides (Dixon, Trans., 1896, **69**, 855), valeryl rhodanide (*ibid.*, 1895, **67**, 1040), caproyl rhodanide (*ibid.*, 1904, **85**, 807), stearyl and palmityl rhodanides (*ibid.*, 1896, **69**, 1593), and phenacetyl rhodanide (*ibid.*, 857) gave with various aryl bases yields of thiocarbamide varying from 60 to nearly 100 per cent. of the theoretical.

Acetyl rhodanide, in fact, may display thiocarbimidic power even in circumstances where phenyl- or allyl-thiocarbimide does not, for, according to our experience, neither of these substances is disposed to unite readily with diphenylamine, whereas the first named combines with it at once.

Acetylthiocarbimide and Diphenylamine.—A solution of the thiocarbimide was prepared by boiling acetyl chloride in benzene with dry lead thiocyanate, and filtering off the lead salts; to this, while hot, was added diphenylamine, dissolved also in boiling benzene. There was vigorous action, and from the solution, on cooling, yellow crystals were deposited, which, after two recrystallisations from spirit, formed long, cream-coloured needles, melting at 141° (corr.). Apart from what remained in the mother liquor, the yield of crude product amounted to 90 per cent. of the theoretical, calculated from the equation:

$$CH_3·CO·NCS + (C_6H_5)_2NH = CH_3·CO·NH·CS·N(C_6H_5)_2.$$

---

* There is no reason to suppose that the dual behaviour of acetyl rhodanide as thiocyanate and thiocarbimide simultaneously is due to the breaking, during interaction, of a complex molecule, $(Ac·CNS)_n$, into simpler components of different constitution, because not only is the moderate boiling point inconsistent with such a view, but, in addition, the molecular weight of a rectified specimen, when determined by Hofmann's method in a steam-jacket, was found to be 104, whilst the calculated value for $C_2H_3O·CNS$ is 101.

The composition was checked by analysis:

0·270 required 20·5 c.c. $N/10$ $BaCl_2$. S = 12·1.
$C_{15}H_{14}ON_2S$ requires S = 11·86 per cent.

The product was nearly insoluble in water, slowly and rather sparingly soluble in hot alcohol, and was gradually desulphurised by boiling with ammoniacal silver nitrate. When boiled with alkaline solution of lead, it seemed at first to undergo no change, but, on continued heating, or by the use of concentrated alkali (1 : 2·5), the mixture was blackened, with formation of lead sulphide. In respect alike of fusibility and of its relations to lead and silver salts, this compound, *a*-acetyl-*bb*-diphenylthiocarbamide, is distinguished very sharply from its isomeride, *a*-acetyl-*ab*-diphenylthiocarbamide, AcNPh·CS·NHPh, a substance melting, according to Deninger (*Ber.*, 1895, **28**, 1322), at 91°, and according to Hugershoff (*Ber.*, 1899, **32**, 3655) at 96°; according to our observations, the latter is desulphurised with ease by these metals, and melts at 96°.

Action of Caustic Alkali on a-*Acetyl*-bb-*diphenylthiocarbamide.*—A quantity of the pure substance, dissolved in alcohol, was heated for an hour on the steam-bath with exactly one equivalent of sodium hydroxide; after standing, the resultant clear solution deposited white crystals, the liquor from which contained sodium acetate. When recrystallised from alcohol, the solid formed large, brilliant, flattened prisms, melting with effervescence to a green liquid at 206—207°, or 212—213° (corr.). Both this and the foregoing compound, when heated with sulphuric acid and a trace of nitric acid, yielded the blue diphenylamine reaction, and were attacked almost explosively by warm nitric acid, the resultant mixture giving with excess of caustic alkali a fine, rose-scarlet coloration. The compound, when dissolved in cold alcohol, yielded with ammoniacal nitrate of silver an immediate black precipitate, but was desulphurised by alkaline lead salts only when the solution was evaporated to a high concentration.

That the above product was *aa*-diphenylthiocarbimide was made certain by digesting it with acetic anhydride on the steam-bath; from the resultant solution, on treatment with alcohol, white crystals were deposited, melting at precisely the same temperature as the preceding *a*-acetyl-*bb*-diphenylthiocarbamide, and, when these two were mixed in equal proportion, the melting point of the mixture was unchanged.

The melting point given by Werner (*loc. cit.*) for *aa*-diphenylthiocarbamide, namely, 198° (presumably uncorr.), appears therefore to be somewhat low. According to our observations, the substance when prepared from diphenylamine, hydrochloric acid, and ammonium thiocyanate had a yellow colour; when this was removed by a few recrystallisations from alcohol, using animal charcoal, it melted at the same temperature as the preceding compound, and, when the two were mixed in equal weights, the melting point remained unaltered, at 206—207° (uncorr.). The temperature of melting depends, however, to some extent on the rate of heating, a fact due, probably, to the occurrence of more or less preliminary decomposition, for if the rate be very slow, a distinct green coloration is visible before melting takes place.

Action of Heat on a-*Acetyl*-bb-*diphenylthiocarbamide.*—A particular interest was attached to the decomposition of this substance by heat, since by dissociation into its constituents it must necessarily yield acetylthiocarbimide,* a compound the properties of which may be compared with those of the acetyl "thiocyanate" resulting from the interaction of acetyl chloride and a metallic thiocyanate.

Thirty grams of the recrystallised thiocarbamide were distilled in a vacuum, the distilling flask being immersed in an oil-bath at about 170°; the oily product, when rectified, formed a clear, straw-yellow liquid, boiling at 30—32° under 9—10 mm. pressure. This substance had the appearance and pungent odour of acetyl "thiocyanate"; it was rapidly hydrolysed by water into acetic and thiocyanic acids, gave with alkaline lead and silver salts, mixtures of sulphide and thiocyanate, and, in short, behaved in every respect like ordinary acetyl "thiocyanate." The various boiling points that have been observed for the latter in different preparations are: 42·25—43°/23 mm. (Hawthorne, *loc. cit.*), 38·25°/19 mm., 37°/17 mm., 50°/34 mm.; if these and the above (say, 31°/9·5 mm.) are plotted on a curve of equal lengths for degrees and mm., the five points lie within the limits of experimental error (1 mm. in the gauge-reading) on a straight line. Further confirmation of the identity was afforded by the index of refraction, μ_D, which measured 1·5237 at 15°, whilst for acetyl "thiocyanate" Hawthorne found at 18·4° the value 1·5232.

The above results are concordant with those obtained in another similar experiment, where *a*-acetyl-*bb*-phenylbenzylthiocarbamide was employed (Dixon, Trans., 1906, **89**, 908), but in the latter case the physical properties of the oil were not subjected to measurement.

It has been mentioned above that acetylthiocarbimide and its congeners gave with most aryl bases good yields of substituted thiocarbamide. But with water, much thiocyanic acid was always produced, and with ammonia, benzylamine, phenylhydrazine, and piperidine the yields of thiocarbamide were poor or almost nothing, and the like was true with respect to succinyldithiocarbimide (Dixon and Doran, Trans., 1895, **67**, 573). Apart therefore from high temperature, which may be a very important factor in determining the direction of change, it would seem that what tends to hinder thiocarbamidic union, and simultaneously to facilitate thiocyanic decomposition, is the use of water, alkalis, or alkaline bases.

---

* Because the acetyl group is attached directly to nitrogen.

Benzoylthiocarbimide.

This substance was prepared by heating together benzoyl chloride, diluted with benzene, and excess of dry lead thiocyanate; when the clear liquor ceased to give the reaction for chlorine, the lead salts were removed by the aid of the pump, and the filtrate was fractionated under diminished pressure.

A sample, thrice rectified, formed a clear, almost colourless oil, boiling at 119° under 10 mm. pressure. Its density at 18·3°/4° was 1·2142, a figure somewhat higher than that given by Miquel (*loc. cit.*), who found 1·197 at 16°; the index of refraction for the *D*-line was 1·6382 at 18·3°, whence $M_D = 85·7$.

This molecular refraction, like that of all other cyclic thiocarbimides hitherto examined, being much higher than the figure calculated by summing the atomic refractions, was compared with the values experimentally determined for phenylthiocarbimide. The figures for the latter, according to Nasini and Scala (*Gazzetta*, 1886, **16**, 70), are $\mu_D = 1·6492$ at 23·4° and $d\frac{23·4°}{4°} = 1·129$, whence $M_D = 77·6$; according to Berliner (*Inaug. Diss.*, Breslau, 1886), $\mu_D = 1·65088$ at 20° and $d\frac{20°}{4°} = 1·1331$, whence $M_D = 77·55$; if to 77·6 be added the refraction-value of C:O, namely, 5·1 + 3·4, or 8·5, the total for $C_6H_5·CO·NCS$ is 86·1, a figure differing by less than 0·5 per cent. from that determined above for benzoylthiocarbimide, namely, 85·7.

Comparison with *o*-tolylthiocarbimide, $C_7H_7·NCS$, gave a similar result, the figures being $\mu_D = 1·6395$ at 16° and $d\frac{16°}{4°} = 1·110$, from which $M_D = 85·8$. This, it may be noted, agrees fairly well with the value, 77·6, for phenylthiocarbimide; thus $77·6 + 5·1(C) + 2·6(H_2) = 85·3$.

If from the molecular refraction of *o*-tolylthiocarbimide, 85·8, there be deducted 2·6 for H_2 and 3·4 be added for :O, the result for

$C_6H_5·CO·NCS$

is 86·6, a figure differing by less than one unit from the number, 85·7, experimentally determined for benzoylthiocarbimide.

Consistently with this, we found that when aniline in toluene solution was dropped into pure benzoylthiocarbimide in toluene at 16—17°, benzoylthiocarbamide was formed without a trace of aniline thiocyanate, and, on repeating this experiment at −70°, the result was precisely the same as at the higher temperature. In the reaction with aniline, therefore, the establishment of low temperature does not develop the capacity of benzoylthiocarbimide to yield thiocyanic products, as it does in the case of acetylthiocarbimide (see p. 686).

Action of Diphenylamine.—According to Miquel (*loc. cit.*, 346), benzoylthiocarbimide could not be caused to unite, even at 200°, with diethylamine or with diphenylamine. Probably something was wrong with the sample of benzoylthiocarbimide employed in these experiments, for it has since been shown (Dixon, Trans., 1896, **69**, 1603) that, in the former case, combination occurs spontaneously, with marked evolution of heat and production of some 90 per cent. of the theoretical yield of *a*-benzoyl-*bb*-diethylthiocarbamide, and it now appears that the like is true as regards union with diphenylamine.

a-Benzoyl-*bb*-diphenylthiocarbamide was produced in a 71 per cent. yield by adding diphenylamine, in benzene solution, to the solution obtained by boiling benzoyl chloride, also in benzene, with lead thiocyanate; when the pure distilled thiocarbimide is employed, the yield of crude product reached 88 per cent. of the theoretical. The substance, when crystallised from alcohol or acetone, formed a white, microcrystalline powder, melting at 135° (corr.), and giving on analysis the following figures:

0·660 required 40·4 c.c. $N/10$ $BaCl_2$. S = 9·8.

$C_{20}H_{16}ON_2S$ requires S = 9·65 per cent.

The compound was soluble in alcohol, benzene, or acetone, and practically insoluble in water. The solution in caustic alkali was blackened very slowly by boiling with a lead salt; the alcoholic solution was not desulphurised by boiling with either neutral or ammoniacal silver nitrate, but was desulphurised by heating with alkali and silver oxide. When treated with sulphuric acid and a trace of nitric acid, or with nitric acid followed by alkali, it gave the blue and rose-scarlet reactions, due to the elimination of diphenylamine.

"*Thiocyanic*" *Behaviour of Benzoylthiocarbimide.*—From the above reactions, and from many others of a like kind, it is plain that benzoylthiocarbimide has properties which serve to establish it as a thiocarbimide and not a thiocyanate. But within certain limits, the same is true of acetyl "thiocyanate"; for example, this substance, when combined with aniline in nearly boiling xylene, gave but 2·5 per cent. of its sulphur as aniline thiocyanate, the remainder forming mainly acetylphenylthiocarbamide, although at −10° this was reversed, some 94 or 95 per cent. appearing as thiocyanate (Dixon and Hawthorne, *loc. cit.*).

These facts suggesting that the difference between acetyl "thiocyanate" and benzoylthiocarbimide is one rather of degree than of kind, indicated the probability that under suitable treatment the latter also might be caused to change, not with production of additive compounds, but of thiocyanic acid instead. Experiment has shown that this is the case.

(i) *Action of Water on Benzoylthiocarbimide.*—Miquel's statement, that benzoylthiocarbimide, when hydrolysed by boiling water, gives benzamide in approximately quantitative yield, we found to be substantially correct. Nevertheless, the aqueous solution, as the oil dissolved, gave with ferric chloride a red coloration, becoming more and more intense, so that, in half an hour or so, the reaction was strongly marked. On conducting a quantitative experiment, and measuring by means of Barnes and Liddles' method with $N/10$ copper sulphate the thiocyanic acid left in solution after the evolution of gas had ceased, we found that of the total ·NCS taken (2·09 grams of pure thiocarbimide), 5 per cent. was present as H·SCN. Therefore the benzoyl group, which is not parted at all from the ·NCS radicle by aniline (see above), is slightly, but distinctly, separated from it by hot water, the main reaction being:

$$PhCO\cdot NCS + H_2O = COS + PhCO\cdot NH_2,$$

and the other, $PhCO\cdot NCS + H_2O = Ph\cdot CO_2H + H\cdot SCN$.

(ii) *Action of Alkali.*—The fact that water alone can separate to some extent the two groups PhCO· and ·NCS, suggested the use of an alkali, since, in the event of partition occurring, the benzoyl would tend to be fixed, and, in so far as the liberated ·NCS might behave as ·SCN, it also would unite to form a stable combination. In testing this, pure distilled benzoylthiocarbimide was heated to boiling with a dilute (2 per cent.) solution of sodium hydroxide, sodium carbonate, or borax, also with lime-water and with magnesium oxide, suspended in water; the product, when acidified and treated with ferric chloride, gave in each case a most intense red coloration. Calcium carbonate and water gave no more coloration than water alone, that is, a faint reddening, the amount of thiocyanic acid so produced being very trifling after some three or four minutes. To ascertain the amount of conversion by alkali, and whether it is dependent on temperature, two experiments were made by allowing the pure thiocarbimide (about 1·6 grams in each case) to dissolve in normal sodium hydroxide at 85° and at 1·5° respectively; when solution was complete, the liquid was neutralised and the contained thiocyanic acid measured by $N/10$ copper sulphate. The former experiment showed of the ·NCS taken, 88·3 per cent. as thiocyanic acid, the latter, 89·9; in both cases some alkali sulphide was present, a portion of the thiocarbimide having undergone the thiocarbimidic hydrolysis into carbonyl sulphide.

Benzoylthiocarbimide, therefore, like acetylthiocarbimide, may undergo the thiocyanic decomposition; that this occurred under the influence of a caustic alkali, suggested the next experiments.

(iii) *Action of Ammonia.*—Ammonia gas or its aqueous solution, according to Miquel (*loc. cit.*, 302), transforms benzoylthiocarbimide quantitatively into the corresponding thiourea. Our experience, so far as the aqueous solution is concerned, does not coincide precisely with this, for we find that, if the oil is shaken with it, benzoylthiocarbamide separates, and the liquor reacts strongly for ammonium thiocyanate. With excess of alcoholic ammonia (about $3N$), we obtained the following results: (*a*) The ammonia was run in at 23—25° to an alcoholic solution of the thiocarbimide (about 3·3 grams), and the resultant mixture filtered from the thiocarbamide, neutralised, and made up with water to a known bulk. By means of $N/10$ copper sulphate, the dissolved thiocyanic acid was measured, and found to contain 51 per cent. of the available sulphur. (*b*) About the same weight as before of thiocarbimide, dissolved in dry toluene, was treated with alcoholic ammonia at $-60°$ to $-70°$; the solvent was then evaporated at the atmospheric temperature, the residue extracted with water, and the dissolved thiocyanate measured as before; this time it contained 54·5 per cent. of the sulphur present in the thiocarbimide. (*c*) Ammonia gas, roughly dried by quicklime, was passed in excess through benzoylthiocarbimide, dissolved in dry benzene; the turbid mixture was then shaken with water, and the aqueous portion separated; when acidified and tested with ferric chloride, it proved to contain a mere trace of thiocyanic acid.

Similar results were obtained with piperidine, *iso*butylamine, and allylamine; these gave in presence of alcohol or moist acetone a considerable amount of thiocyanic acid, but in presence of dry benzene, little or practically none.

With benzoylthiocarbimide, therefore, what happens appears to depend largely on what is presented to it, and on whether or not water is present; alkaline substances in presence of moisture hydrolysing it freely, but in the absence of water having little power in this direction.

Aryl bases, which (save in the case of aniline) produce with acetylthiocarbimide an inconsiderable amount of thiocyanic acid, with benzoylthiocarbimide give none at all; the function of the ·NCS group in benzoylthiocarbimide, however, unlike that in the acetyl congener, appears to be uninfluenced, at least for practical purposes, by the temperature at which a base is presented for interaction.

On the whole, however, it now appears that there is little difference between acetyl "thiocyanate" and benzoyl "thiocarbimide," save as regards the ease with which they undergo thiocyanic change by hydrolysis, seeing that acetyl thiocyanate may behave largely as a thiocarbimide and benzoyl thiocarbimide as a thiocyanate. We are of opinion, therefore, that true acetyl thiocyanate remains still to be discovered, and that Hawthorne's view (*loc. cit.*) is correct, that acetyl rhodanide is a thiocarbimide. In the same sense, that is, as benzoyl thiocarbimide, in other words, that so far as either of them yields the products of a thiocyanate, this is due to hydrolytic separation of the constituent radicles,* with subsequent change of the ·NCS to ·SCN. The same applies, of course, to propionyl, butyryl, stearyl, and other "thiocyanates" of the aliphatic class, and probably to all rhodanides of strongly electronegative radicles; whether the thiocyanates of negative inorganic radicles, such as phosphorus, phosphoryl, &c., are also thiocarbimidic, is a subject which we propose next to investigate.

Carboxymethylthiocarbimide.

Derivatives of carboxymethylthiocarbimide have been described by Doran (Trans., 1901, **79**, 906), who, however, did not isolate the parent compound. The difficulty which he sometimes experienced in effecting complete interaction between methyl chlorocarbonate and lead thiocyanate in boiling benzene, or toluene, or mixtures of both, we verified, having failed to obtain more than traces of the desired product after several hours' heating. By addition of the chlorocarbonate to a hot saturated solution of potassium thiocyanate in nearly dry acetone, the difficulty was overcome, potassium chloride being precipitated instantly; the mixture was then allowed to cool, filtered, and the filtrate distilled under diminished pressure.

By operating thus, carboxymethylthiocarbimide was obtained as a clear, almost colourless oil, having an exceedingly pungent odour, most irritating to the eyes and nose; after rectification, it boiled at 30° under 12 mm. pressure. The density at 15°/4° was 1·152, and the refractive index for the *D*-line, 1·48862 at 15°; from these figures, the molecular refraction is 49·6.

The substance differs by one oxygen atom from acetylthiocarbimide; if to Hawthorne's value for this (*loc. cit.*), namely, 46·1 at 15°, the figure, 3·1, for "ether" oxygen be added, the total, 49·2, lies not far from the above experimental number; it seems probable, therefore, that carboxymethylthiocarbimide is similar in constitution to acetyl "thiocyanate."

---

* The hydrolysis of benzoyl chloride by water occurs much less readily than that of acetyl chloride.

No quantitative chemical experiments were made with carboxymethylthiocarbimide and bases, alkalis, &c., but qualitatively it agreed so closely in every way with benzoylthiocarbimide that the description already given of the latter may serve for the carboxymethyl compound.

Action of Diphenylamine.—Carboxymethylthiocarbimide united readily with diphenylamine in hot benzene, the product, after two recrystallisations from alcohol, forming rosettes of prisms, melting at 128—129° (corr.):

0·572 required 40·4 c.c. *N*/10 $BaCl_2$. S = 11·3.

$C_{15}H_{14}O_2N_2S$ requires S = 11·19 per cent.

The trisubstituted thiocarbamide was practically insoluble in water, and soluble in chloroform or benzene. Its solution in caustic alkali was slowly blackened when boiled with a lead salt; the alcoholic solution was unaffected by boiling with alcoholic silver nitrate, and this mixture when treated with ammonia was not disulphurised, but a white silver compound separated in brilliant needles.

a-*Carboxymethyl*-ab-*diphenylthiocarbimide.*—For the purpose of comparison, this isomeride of the preceding compound was prepared by mixing methyl chlorocarbonate with alcoholic thiocarbanilide. The product, when twice recrystallised, formed long, flattened prisms, melting at 106°. The alcoholic solution was readily desulphurised by warming with neutral silver nitrate or alkaline salts of lead:

0·572 required 40·5 c.c. *N*/10 $BaCl_2$. S = 11·3.

$C_{15}H_{14}O_2N_2S$ requires S = 11·19 per cent.

Carboxyethylthiocarbimide.

This compound has already been isolated by Doran (Trans., 1896, **69**, 335), who gives the boiling point 66—67°/21 mm. As in the case of the carboxymethyl homologue, we found the preparation from lead thiocyanate to be tedious and unsatisfactory, and therefore used the potassium thiocyanate and acetone process described on p. 696. When purified by fractionation, the substance boiled at about 83° under a pressure of 30 mm.; it tends, however, to decompose somewhat, with evolution of carbon dioxide and desulphuretted gases. Under 14 mm., the boiling point of a rectified specimen was found to be about 43°; if plotted as before, these three figures lie on a straight line.

The density at 15°/4° was 1·112, and μ_D at 15° was 1·47985, from which $M_D = 56·5$. On comparing this, as before, with the carefully determined value, 46·1, of the acetyl congener, and adding thereto the values of ·O· and of CH_2 (namely, 3·1 and 5·1 + 2·6, or 10·8), the total is 56·9, a number so close to that found experimentally as to leave little room for doubt as to the similarity of both compounds as regards the union of the ·NCS group.

From Doran's results with this carboxyethyl compound there can be no doubt as to its thiocarbimidic nature, since even with ammonia and fatty bases it produces the corresponding thiocarbamides, and generally in good yield.

Nevertheless, it can furnish a considerable amount of thiocyanic acid under the right conditions, which are those already described for the benzoyl and carboxymethyl analogues. When boiled with alkaline lead tartrate, well-marked desulphurisation occurs, and the same is true as regards alcoholic silver nitrate; in neither case, however, is the production of sulphide anything like quantitative, the mixture containing always much thiocyanate.

How strongly caustic alkali determines the latter form of change was shown by digesting 0·432 gram of the purified oil with excess (40 c.c.) of normal sodium hydroxide. After half an hour, when all was dissolved, the solution was neutralised and the thiocyanate determined as before with *N*/10 copper sulphate; it accounted for nearly 93 per cent. of the total sulphur present.

Action of Diphenylamine.—Prepared as before, the trisubstituted thiocarbamide formed brilliant, short, thick, rhombic prisms, practically insoluble in water, moderately soluble in alcohol or acetone, readily so in benzene or hot caustic alkali, and melted, when slowly heated, at 125—125·5° (corr.):

0·6 required 40·5 c.c. *N*/10 $BaCl_2$. S = 10·8.

$C_{16}H_{16}O_2N_2S$ requires S = 10·66 per cent.

The compound was scarcely affected by ammoniacal silver nitrate even on prolonged boiling in presence of alcohol, and the solution in alkali, when heated with a lead salt, was not blackened until the mixture was boiled down almost to fusion.

Most sharp is the contrast between this resistance and the ready desulphurisation by these reagents of the isomeride

$$PhN(CO_2Et){\cdot}CS{\cdot}NHPh$$

of Seidel (*J. pr. Chem.*, 1885, [ii], **32**, 263), which melts at 95°.

Johnson, who has worked considerably of late on the acidic "thiocyanates," considers that in all cases where a thiocarbimide is found as the product of the reaction between an acyl chloride and a metallic thiocyanate, the thiocarbimide originates through the transformation of a thiocyanate initially formed, and gives in support of this view (*Amer. Chem. J.*, 1907, **38**, 456) an instance of the production of diphenylcarbamyl thiocyanate and of its direct conversion by heating into diphenylcarbamylthiocarbimide, a substance already obtained by one of us (Dixon, Trans., 1899, **75**, 393) from the corresponding chloride and mercuric thiocyanate in boiling cumene. In the paper cited, he predicts that other similar chlorides may be caused to furnish thiocyanates as well as thiocarbimides.

In view of the properties of these particular chlorides, it seems very probable that Johnson's anticipation may be verified. The electronegative character of diphenylcarbamyl chloride, for example, is so feebly marked that it may be crystallised unchanged from alcohol; the corresponding *aa*-diphenylurea is obtained by heating it with alcoholic ammonia in a sealed tube at 100°, and to bring about its reaction with aniline the two are heated together in chloroform at 130°; in short, this chloride behaves in many ways more like an alkylogen than like an ordinary acylogen. Johnson points out that this is the first occasion on which an acyl thiocyanate has definitely been isolated having no thiocarbimidic characters (as measured by the power to unite additively with nitrogenous bases) until transformed by heat; the case, therefore, is distinctly interesting; nevertheless, it does not follow from these results that highly electronegative acid chlorides must behave in the same way with metallic thiocyanates, giving two distinct compounds, or that the product must be first thiocyanate and then thiocarbimide by transposition.

The conclusion which from the facts now available we draw with regard to the acyl "thiocyanates" is, that such compounds are still unknown, the products resulting from the interaction of metallic thiocyanates and acylogens, at least in all cases where the acyl group is pronouncedly electronegative, being thiocarbimidic in constitution. In one respect, however, these substances differ from the hydrocarbon thiocarbimides somewhat as the amides from the amines, namely, as regards the former being subject to hydrolytic change with loss of nitrogen, for whilst the amides, by elimination of the NH_2 group with hydrogen, yield ammonia, so the acylthiocarbimides, by loss of ·NCS with hydrogen, yield thiocyanic acid. And, just as with the amides, caustic alkalis tend to determine this kind of hydrolysis, so with the acylthiocarbimides, all forms of which appear to be susceptible of the corresponding change.

Considerable differences exist in respect of the ease with which such hydrolysis may occur; thus, water alone determines it almost quantitatively for the thiocarbimides of aliphatic acids, whereas with those of aromatic acids, or even aryl-substituted aliphatic acids, or the less electronegative oxy-aliphatic series, the hydrolysis is far from complete.

Generally speaking, the thiocarbimidic function, as measured by the power to unite additively with nitrogenous bases, is best developed in the cases where thiocyanic hydrolysis does not readily occur; but even here, as might be expected, with caustic alkalis, and especially in presence of ionising solvents, the thiocyanic behaviour may be very well marked.

In cases where a nitrogenous base is disposed to cause the thiocyanic decomposition of a thiocarbimide, increase of the temperature of interaction is a most potent factor in hindering it, and determining additive, or thiocarbimidic, change instead; why this should be, we do not know.

In conclusion, another curious point may be noted. A hydrocarbon thiocarbimide, X·NCS, may be united with a similar base, $Y{\cdot}NH_2$, the corresponding combination of Y·NCS with $X{\cdot}NH_2$ being equally practicable. On the other hand, if X is an acyl group and Y an aryl, reaction occurs readily enough, whereas the combination of a hydrocarbon thiocarbimide with an amide, such as acetamide, seems impossible to be accomplished. But if the arylthiocarbimide be first combined with ammonia, the resultant thiocarbamide,

$$X{\cdot}NH{\cdot}CS{\cdot}NH_2,$$

may ultimately be converted by an acylogen or an acid anhydride into the disubstituted thiocarbamide. It is noteworthy, however, that in neither of these two latter actions is the conversion direct, the acyl group migrating at least once, and it may be twice, in the new molecule before the symmetrical configuration is attained.

CHEMICAL DEPARTMENT,
QUEEN'S COLLEGE,
CORK.

LXV.—*The Relation between Unsaturation and Optical Activity. Part II. Alkaloid Salts of Corresponding Saturated and Unsaturated Acids.*

By THOMAS PERCY HILDITCH.

IN Part I of this series (Trans., 1908, **93**, 1) it was shown that in the case of menthyl and bornyl esters of β-phenylpropionic, cinnamic, and phenylpropiolic acids the ethylenic esters possessed greater optical activity than the saturated compounds, whilst the acetylenic derivatives, on the other hand, showed less optical activity than even the latter. It also appeared that the effect of unsaturation was modified by the constitution of the optically active part of the molecule, and, in order to throw more light on this point, esters of a series of fatty acids are being prepared. The examination of these is not yet complete, but in the meantime a number of salts of these various acids with certain optically active alkaloids has been investigated, and the results obtained show clearly that the effect of unsaturation varies, not only with the optically active part of the molecule, but also with the type of acid used.

Compounds of the alkaloids do not seem to have been used very extensively in work of this nature, possibly because of the complicated structure of such bodies, but many of them possess a large rotatory power and thus are very suitable for the purpose. Minguin (*Compt. rend.*, 1905, **140**, 243) has investigated the effect of the addition of equivalent amounts of many organic acids on the activity of a solution of strychnine in a mixture of benzyl and ethyl alcohols. Amongst these are succinic, maleic, fumaric, and butyric and crotonic acids, and in these cases the ethylenic acid exerted a larger effect on the rotatory power.

The alkaloids used in the work now described were brucine, coniine, codeine, and cinchonine, and the rotatory powers of the salts of these with β-phenylpropionic, cinnamic, and phenylpropiolic, and succinic, maleic, fumaric, and acetylenedicarboxylic acids have been measured. It is a well-known rule that such salts, if examined in aqueous solution, show a rotation which tends to a constant value for each alkaloid (Oudemans, *Annalen*, 1876, **182**, 33, 58), but by measuring the optical activity in non-ionising media it is possible to obtain the rotatory power due to each individual salt. The solvent generally used was dry chloroform; in a few cases it was necessary to have recourse to alcohol or acetone, but, as a rule, the salts were sufficiently soluble in the first-named solvent.

The rotation of each salt when dissolved in water has also been measured; the molecular rotations found are not by any means the same for a given alkaloid, and do not, as a rule, agree well with those previously determined from the salt of the alkaloids and a strong acid, such as hydrochloric or nitric acid. It should be mentioned, however, that salts of the alkaloids and weak organic acids have not been investigated from this point of view, and it is possible that, as discussed later, hydrolysis of the salts takes place and that this introduces a disturbing factor into the problem.

The opportunity has been taken to observe the relative effects of the maleinoid and fumaroid forms of ethylenic dicarboxylic acids on optical activity. Walden (*Zeitsch. physikal. Chem.*, 1896, **20**, 377) observed that in the case of the diamyl esters of fumaric and maleic, chlorofumaric and chloromaleic, and bromofumaric and bromomaleic acids, the fumaroid form possessed the greater rotatory power, but Hartwall (*Diss.*, Helsingfors, 1904) found the reverse rule to hold for the acid and neutral bornyl esters of fumaric and maleic acids, although with both menthyl and bornyl acid, citraconates, and mesaconates the fumaroid esters possessed greater optical effect. Hence it would appear that in this case, also, no absolutely fixed rule covers all conditions, and the data now afforded by these alkaloid salts must therefore be of interest.

The brucine salts were prepared by mixing equivalent quantities of base and acid in boiling water, filtering, and cooling. As a rule, the compounds separated at once on cooling in magnificent crystals, but in one or two cases it was found advisable to evaporate the solution to a syrup and cover with ether, when crystallisation set in at once. The salts were sufficiently pure after one recrystallisation from water.

The coniine, codeine, and cinchonine salts did not separate so well from water, and were prepared by mixing equivalent amounts of the constituents in chloroform and evaporating in a vacuum at the ordinary temperature. In this way, most of the salts were obtained crystalline at once, but a few of them solidified only with difficulty.

The rotations were measured in a 2-dcm. polarimeter tube, and, where possible, at three concentrations (approximately 4, 2, and 1 per cent.) in each solvent used. In a few cases, however, the maximum concentration possible was less than 1 per cent.

The optical activity of each alkaloid used was measured previous to, and after use in, the experiments; an account of these, together with a brief description of the properties of the salts, will now be given.

I. *Brucine Salts.*

The brucine used for these experiments melted at 178° before use, and at 179° after recovery from the salts, and its optical activity when tested in dry chloroform solution was as follows:

Percentage concentration.	Before use.				After use.			
	Temp.	α.	$[\alpha]_D$.	$[M]_D$.	Temp.	α.	$[\alpha]_D$.	$[M]_D$.
4	23°	−9·76	−122·0	−480·7	26°	−9·42	−117·75	−463·8
2	,,	4·86	121·5	478·6	,,	4·72	118·0	464·9
1	,,	2·40	120·0	472·9	,,	2·50	125·0	492·5

Brucine β-Phenylpropionate, $C_{23}H_{26}O_4N_2,C_9H_{10}O_2,3H_2O$.

Thin prisms, sparingly soluble in water, readily so in alcohol, melting at 90° (hydrated salt):

0·0996 anhydrous salt gave 0·2584 CO_2 and 0·0587 H_2O. C = 70·76; H = 6·55.

0·2373 anhydrous salt required 4·40 c.c. *N*/10 KOH. $C_9H_{10}O_2 = 27·82$.

$C_{32}H_{36}O_6N_2$ requires C = 70·59; H = 6·62; $C_9H_{10}O_2 = 27·57$ per cent.

0·2609 hydrated salt lost 0·0236 at 100°. $H_2O = 9·05$.

$C_{32}H_{36}O_6N_2,3H_2O$ requires $H_2O = 9·02$ per cent.

(The salts were titrated by adding a known volume of standard potassium hydroxide, shaking with chloroform to remove brucine, and then titrating back the aqueous layer with standard acid):

Solvent.	Percentage concentration.	Temp.	α.	[α]D.	[M]D.
Chloroform	3·64	19°	−2·78	−38·19	−207·7
,, ...	1·82	19	1·40	38·46	209·2
,, ...	0·91	19	0·70	38·46	209·2
Water	0·91	19	−0·46	−25·27	−137·5

Brucine Cinnamate, $C_{23}H_{26}O_4N_2,C_9H_8O_2,3H_2O$.

This salt, prepared from synthetic cinnamic acid, crystallised in small tablets, slightly soluble in cold water, and readily so in alcohol. The hydrated salt melted sharply at 113°. No signs of other salts, such as those mentioned by Erlenmeyer, jun. (*Ber.*, 1905, **38**, 3499; 1906, **39**, 285, 1570), were observed, and, since the compound obtained melts at the same temperature as that referred to by Marckwald and Meth (*Ber.*, 1906, **39**, 1171) as containing one molecule of alcohol of crystallisation, it is probable that both compounds become anhydrous before reaching the melting point:

0·1329 gave 0·3134 CO_2 and 0·0846 H_2O. C = 64·31; H = 7·07.

0·1517 lost 0·0142 at 100°. H_2O = 9·36.

$C_{32}H_{34}O_6N_2,3H_2O$ requires C = 64·43; H = 6·71; H_2O = 9·06 per cent.

0·1375 anhydrous salt required 2·61 c.c. *N*/10 KOH. $C_9H_8O_2$ = 27·99.

$C_{32}H_{34}O_6N_2$ requires $C_9H_8O_2$ = 27·31 per cent.

Solvent.	Percentage concentration.	Temp.	α.	[α]D.	[M]D.
Chloroform	3·64	18°	−0·85	−11·68	−63·3
,, ...	1·82	18	0·50	13·74	74·5
,, ...	0·91	18	0·32	17·58	95·4
Water	0·91	19	−0·34	−18·68	−101·3

Brucine Phenylpropiolate, $C_{23}H_{26}O_4N_2,C_9H_6O_2,2H_2O$.

Short, slender needles, contracting at 100—110°, and melting with decomposition at 155°:

0·0995 gave 0·2435 CO_2 and 0·0577 H_2O. C = 66·82; H = 6·45.

0·1042 lost 0·0064 at 100°. H_2O = 6·14.

$C_{32}H_{32}O_6N_2,2H_2O$ requires C = 66·67; H = 6·25; H_2O = 6·25 per cent.

0·1956 anhydrous salt required 3·70 c.c. *N*/10 KOH. $C_9H_6O_2$ = 27·63.

$C_{32}H_{32}O_6N_2$ requires $C_9H_6O_2$ = 27·04 per cent.

Solvent.	Percentage concentration.	Temp.	α.	[α]D.	[M]D.
Chloroform	3·75	19°	+0·25	+3·33	+18·0
,, ...	1·88	19	0·12	3·20	17·3
,, ...	0·94	19	0·05	2·67	14·4
Water	0·94	19	−0·43	−22·94	−123·8

Brucine Hydrogen Succinate, $C_{23}H_{26}O_4N_2,C_4H_6O_4,2H_2O$.

White needles, fairly soluble in water, very sparingly so in organic solvents, melting with decomposition at 218°:

0·1994 gave 0·4296 CO_2 and 0·1220 H_2O. C = 58·75; H = 6·80.

0·2118 lost 0·0136 at 100°. H_2O = 6·42.

$C_{27}H_{32}O_8N_2,2H_2O$ requires C = 59·12; H = 6·57; H_2O = 6·57 per cent.

0·1982 anhydrous salt required 7·55 c.c. *N*/10 KOH. $C_4H_6O_4$ = 22·48.

$C_{27}H_{32}O_8N_2$ requires $C_4H_6O_4$ = 23·04 per cent.

Solvent.	Percentage concentration.	Temp.	a.	$[a]_D$.	$[M]_D$.
Chloroform	0·47	25°	−0·22	−23·40	−119·9
Alcohol................	0·47	25	−0·30	−31·92	−163·4
Water	3·74	24	−2·08	−27·81	−142·4
,, ...	1·87	24	1·00	26·74	137·0
,, ...	0·94	24	0·46	24·60	126·0

Brucine Hydrogen Maleate, $C_{23}H_{26}O_4N_2,C_4H_4O_4,\frac{1}{2}H_2O$.

White, glistening crystals, sparingly soluble in all solvents, decomposing at 240—245°:

0·1453 gave 0·3307 CO_2 and 0·0810 H_2O. C = 62·05; H = 6·19.

0·3333 required 13·00 c.c. *N*/10 KOH. $C_4H_4O_4$ = 22·60.

$C_{27}H_{30}O_8N_2,\frac{1}{2}H_2O$ requires C = 62·41; H = 5·97; $C_4H_4O_4$ = 22·35 per cent.

Solvent.	Percentage concentration.	Temp.	a.	$[a]_D$.	$[M]_D$.
Chloroform	0·49	25°	+0·06	+6·12	+31·2
Water	0·98	25	−0·48	−24·49	−124·9

Brucine Hydrogen Fumarate, $C_{23}H_{26}O_4N_2,C_4H_4O_4,2H_2O$.

White prisms, insoluble in chloroform, sparingly so in other solvents, melting at 189°:

0·1140 gave 0·2490 CO_2 and 0·0621 H_2O. C = 59·57; H = 6·05.

0·2022 lost 0·0057 at 100° and required 7·40 c.c. *N*/10 KOH. H_2O = 2·82; $C_4H_4O_4$ = 21·22.

$C_{27}H_{30}O_8N_2,2H_2O$ requires C = 59·34; H = 6·23; $1H_2O$ = 3·29; $C_4H_4O_4$ = 21·24 per cent.

Solvent.	Percentage concentration.	Temp.	a.	$[a]_D$.	$[M]_D$.
Alcohol...............	0·47	23°	+0·10	+10·69	+54·5
Water	1·87	24	−0·93	−24·86	−126·9
,, ...	0·94	24	0·47	25·14	128·2

Brucine Hydrogen Acetylenedicarboxylate, $C_{23}H_{26}O_4N_2,C_4H_2O_4,3\frac{1}{2}H_2O$.

White, crystalline powder, fusing at 90°, solidifying again, and finally melting with foaming at 165°:

0·1360 gave 0·2842 CO_2 and 0·0791 H_2O. C = 56·99 ; H = 6·46.

0·2058 lost 0·0221 at 100° and required 7·05 c.c. *N*/10 KOH. H_2O = 10·74 ; $C_4H_2O_4$ = 19·53.

$C_{27}H_{28}O_8N_2,3\frac{1}{2}H_2O$ requires C = 56·74 ; H = 6·12 ; H_2O = 11·03 ; $C_4H_2O_4$ = 19·97 per cent.

Solvent.	Percentage concentration.	Temp.	α.	[α]$_D$.	[M]$_D$.
Chloroform	0·47	27°	− 0·05	− 5·36	− 27·2
Alcohol	0·47	27	− 0·03	− 3·22	− 16·4
Water	3·73	25	− 1·12	− 15·02	− 76·3
,,	1·87	25	0·77	20·65	104·9
,,	0·93	25	0·35	18·77	95·4

Brucine Succinate, $(C_{23}H_{26}O_4N_2)_2,C_4H_6O_4,7H_2O$.

Clusters of needles, soluble in water and chloroform, very sparingly so in acetone and alcohol, melting at 151° :

0·1511 gave 0·3209 CO_2 and 0·0993 H_2O. C = 57·92 ; H = 7·30.

0·3681 lost 0·0473 at 100° and required 7·20 c.c. *N*/10 KOH. H_2O = 12·85 ; $C_4H_6O_4$ = 11·54.

$C_{50}H_{58}O_{12}N_4,7H_2O$ requires C = 58·14 ; H = 6·98 ; H_2O = 12·21 ; $C_4H_6O_4$ = 11·43 per cent.

Solvent.	Percentage concentration.	Temp.	α.	[α]$_D$.	[M]$_D$.
Chloroform	4	23°	− 5·50	− 68·75	− 622·9
,,	2	23	2·93	73·25	663·6
,,	1	23	1·51	75·50	683·9
Water	4	25	− 2·70	− 33·75	− 305·8
,,	2	25	1·35	33·75	305·8
,,	1	25	0·64	32·00	289·9

Brucine Maleate, $(C_{23}H_{26}O_4N_2)_2,C_4H_4O_4,7\frac{1}{2}H_2O$.

Quill-like crystals, fusing at 100—105°, resolidifying, and finally melting at 181° :

0·1811 gave 0·3828 CO_2 and 0·1144 H_2O. C = 57·65 ; H = 7·02.

0·1778 lost 0·0227 at 100°. H_2O = 12·76.

$C_{50}H_{56}O_{12}N_4,7\frac{1}{2}H_2O$ requires C = 57·77 ; H = 6·83 ; H_2O = 13·09 per cent.

0·1551 anhydrous salt required 3·50 c.c. *N*/10 KOH. $C_4H_4O_4$ = 13·09.

$C_{50}H_{56}O_{12}N_4$ requires $C_4H_4O_4$ = 12·83 per cent.

Solvent.	Percentage concentration.	Temp.	α.	[α]$_D$.	[M]$_D$.
Chloroform	1·74	24°	− 2·20	− 63·22	− 571·5
,,	0·87	24	1·07	61·51	556·0
Water	3·48	23	− 3·13	− 44·97	− 406·5
,,	1·74	23	1·48	42·53	384·5
,,	0·87	23	0·73	41·96	379·3

Brucine Fumarate, $(C_{23}H_{26}O_4N_2)_2,C_4H_4O_4,6H_2O$.

White needles, sparingly soluble in alcohol and acetone, more soluble in chloroform and water, melting at 174°:

0·1071 gave 0·2330 CO_2 and 0·0660 H_2O. C = 59·33; H = 6·85.

0·1626 lost 0·0169 at 100° and required 3·1 c.c. *N*/10 KOH. H_2O = 10·40; $C_4H_4O_4$ = 11·06.

$C_{50}H_{56}O_{12}N_4,6H_2O$ requires C = 59·30; H = 6·72; H_2O = 10·67; $C_4H_4O_4$ = 11·46 per cent.

Solvent.	Percentage concentration.	Temp.	α.	$[\alpha]_D$.	$[M]_D$.
Chloroform	1·79	24°	− 2·20	− 61·45	− 555·5
,, ...	0·90	24	1·12	62·58	565·7
Water	1·79	22	− 1·25	− 34·91	− 315·6
,, ...	0·90	22	0·62	34·64	313·2

Brucine Acetylenedicarboxylate, $(C_{23}H_{26}O_4N_2)_2,C_4H_2O_4,10H_2O$.

Small, white crystals, sparingly soluble in alcohol and acetone, readily so in chloroform and water. The hydrated salt melts at 105—106°, and the anhydrous salt at 169°. After drying at 100°:

0·1402 gave 0·3367 CO_2 and 0·0766 H_2O. C = 65·49; H = 6·07.

0·1637 required 3·70 c.c. *N*/10 KOH. $C_4H_2O_4$ = 12·88.

$C_{50}H_{54}O_{12}N_4,H_2O$ requires C = 65·22; H = 6·09; $C_4H_2O_4$ = 12·39 per cent.

0·3557 hydrated salt lost 0·0514 at 100°. H_2O = 14·45.

$C_{50}H_{54}O_{12}N_4,10H_2O$ requires $9H_2O$ = 14·97 per cent.

Solvent.	Percentage concentration.	Temp.	α.	$[\alpha]_D$.	$[M]_D$.
Chloroform	3·34	23°	− 4·12	− 61·67	− 556·3
,, ...	1·67	23	2·34	70·06	632·0
,, ...	0·84	23	1·17	70·06	632·0
Water	3·34	22	− 2·00	− 29·93	− 270·1
,, ...	1·67	22	1·00	29·93	270·1
,, ...	0·84	22	0·48	28·74	259·2

II. *Coniine Salts.*

The coniine used boiled at 166°, and its rotatory power in chloroform solution, before use and after recovery from the salts, is given below:

Percentage concentration.	Before use.				After use.			
	Temp.	α.	$[\alpha]_D$.	$[M]_D$.	Temp.	α.	$[\alpha]_D$.	$[M]_D$.
4	27°	+ 0·64	+ 8·00	+ 10·16	23°	+ 0·61	+ 7·63	+ 9·69
2	27	0·34	8·50	10·80	23	0·30	7·50	8·27
1	27	0·18	9·00	11·43	23	0·17	8·50	10·80

Coniine β-Phenylpropionate, $C_8H_{17}N,C_9H_{10}O_2$.

Very small, deliquescent, cubical crystals:

0·1558 gave 0·4186 CO_2 and 0·1318 H_2O. C = 73·26; H = 9·40.

$C_{17}H_{27}O_2N$ requires C = 73·64; H = 9·75 per cent.

Solvent.	Percentage concentration.	Temp.	α.	$[\alpha]_D$.	$[M]_D$.
Chloroform	4	27°	−0·15	−1·87	−5·18
,, ...	2	27	0·07	1·75	4·85
,, ...	1	27	0·04	2·00	5·54
Water	4	24	+0·20	+2·50	+6·93

Coniine Cinnamate, $C_8H_{17}N,C_9H_8O_2$.

Slender, white needles, melting at 82—83°, soluble in water and organic solvents:

0·1313 gave 0·3576 CO_2 and 0·1059 H_2O. C = 74·27; H = 8·96.

$C_{17}H_{25}O_2N$ requires C = 74·18; H = 9·09 per cent.

Solvent.	Percentage concentration.	Temp.	α.	$[\alpha]_D$	$[M]_D$.
Chloroform	4	22°	−0·60	−7·50	−20·6
,, ...	2	22	0·30	7·50	20·6
,, ...	1	22	0·17	8·50	23·4
Water	4	24	+0·14	+1·75	+ 4·8

Coniine Phenylpropiolate, $C_8H_{17}N,C_9H_6O_2$.

Stout prisms, soluble in most solvents, melting at 107°:

0·1798 gave 0·4955 CO_2 and 0·1403 H_2O. C = 75·13; H = 8·67.

$C_{17}H_{23}O_2N$ requires C = 74·73; H = 8·46 per cent.

Solvent.	Percentage concentration.	Temp.	α.	$[\alpha]_D$.	$[M]_D$.
Chloroform	4	21°	−0·57	−7·12	−19·4
,, ...	2	21	0·27	6·75	18·4
,, ...	1	21	0·14	7·00	19·1
Water	4	24	+0·08	+1·00	+2·7

Coniine Succinate, $(C_8H_{17}N)_2,C_4H_6O_4$.

Feathery needles deposited very slowly from a viscous oil:

0·1265 gave 0·2980 CO_2 and 0·1201 H_2O. C = 64·24; H = 10·54.

$C_{20}H_{40}O_4N_2$ requires C = 64·52; H = 10·75 per cent.

Solvent.	Percentage concentration.	Temp.	α.	$[\alpha]_D$.	$[M]_D$.
Chloroform	4	22°	+0·41	+5·12	+19·0
,, ...	2	22	0·20	5·00	18·6
,, ...	1	22	0·10	5·00	18·6
Water	4	24	+0·12	+1·50	+5·6

Coniine Maleate, $(C_8H_{17}N)_2,C_4H_4O_4$.

Small, deliquescent prisms, readily soluble in organic solvents:

0·1404 gave 0·3320 CO_2 and 0·1300 H_2O. C = 64·48; H = 10·34.

$C_{20}H_{38}O_4N_2$ requires C = 64·86; H = 10·27 per cent.

Solvent.	Percentage concentration.	Temp.	a.	[a]_D.	[M]_D.
Chloroform	4	18°	+0·35	+4·38	+16·2
,, ...	2	18	0·19	4·75	17·6
,, ...	1	18	0·09	4·50	16·6
Water	4	24	+0·16	+2·00	+7·4

Coniine Fumarate, $(C_8H_{17}N)_2,C_4H_4O_4$.

Deliquescent crystals, soluble in most ordinary solvents:

0·1701 gave 0·4040 CO_2 and 0·1600 H_2O. C = 64·79; H = 10·46.

$C_{20}H_{38}O_4N_2$ requires C = 64·86; H = 10·27 per cent.

Solvent.	Percentage concentration.	Temp.	a.	[a]_D.	[M]_D.
Chloroform	4	22°	+0·32	+4·00	+14·8
,, ...	2	22	0·17	4·25	15·7
,, ...	1	22	0·09	4·50	16·6
Water	4	24	+0·14	+1·75	+6·5

Coniine Acetylenedicarboxylate, $(C_8H_{17}N)_2,C_4H_2O_4$.

Long, colourless needles, readily soluble in organic solvents:

0·1226 gave 0·2905 CO_2 and 0·1117 H_2O. C = 64·62; H = 10·12.

$C_{20}H_{36}O_4N_2$ requires C = 65·22; H = 9·78 per cent.

Solvent.	Percentage concentration.	Temp.	a.	[a]_D.	[M]_D.
Chloroform	4	22°	+0·27	+3·37	+12·4
,, ...	2	22	0·14	3·50	12·9
,, ...	1	22	0·08	4·00	14·7
Water	4	24	+0·08	+1·00	+3·7

III. *Codeine Salts.*

The specimen of codeine used melted at 154° before use, and at 153—154° after recovery from the salts; its optical rotatory power was measured as usual in dry chloroform solution:

Percentage concentration.	Before use.				After use.			
	Temp.	a.	[a]_D.	[M]_D.	Temp.	a.	[a]_D.	[M]_D.
4	23°	−9·25	−115·63	−366·6	22°	−9·12	−114·00	−361·4
2	23	4·50	112·50	356·7	22	4·46	111·50	353·5
1	23	2·33	116·50	369·3	22	2·31	115·50	365·1

Codeine β-Phenylpropionate, $C_{18}H_{21}O_3N,C_9H_{10}O_2$.

White, prismatic crystals, readily soluble in chloroform and water, sparingly so in ether:

0·0943 gave 0·2492 CO_2 and 0·0600 H_2O. C = 72·07; H = 7·07.

$C_{27}H_{31}O_5N$ requires C = 72·16; H = 6·91 per cent.

Solvent.	Percentage concentration.	Temp.	α.	[α]D.	[M]D.
Chloroform	4	24°	−5·15	−64·37	−289·0
,, ...	2	24	2·57	64·25	288·4
,, ...	1	24	1·27	63·35	284·4
Water	1	22	−1·76	−88·00	−395·1

Codeine Cinnamate, $C_{18}H_{21}O_3N,C_9H_8O_2$.

Clusters of white crystals, melting at 50°:

0·0954 gave 0·2553 CO_2 and 0·0595 H_2O. C = 72·95; H = 6·93.

$C_{27}H_{29}O_5N$ requires C = 72·47; H = 6·49 per cent.

Solvent.	Percentage concentration.	Temp.	α.	[α]D.	[M]D.
Chloroform	4	23°	−4·13	−51·63	−230·7
,, ...	2	23	2·08	52·00	232·5
,, ...	1	23	1·05	52·50	234·7
Water	1	22	−1·50	−75·00	−335·3

Codeine Phenylpropiolate, $C_{18}H_{21}O_3N,C_9H_6O_2$.

Hard, white prisms, melting at 63°:

0·1377 gave 0·3701 CO_2 and 0·0806 H_2O. C = 73·28; H = 6·50.

$C_{27}H_{27}O_5N$ requires C = 72·80; H = 6·07 per cent.

Solvent.	Percentage concentration.	Temp.	α.	[α]D.	[M]D.
Chloroform	4	23°	−4·08	−51·00	−227·0
,, ...	2	23	1·99	49·75	221·4
,, ...	1	23	1·01	50·50	224·8
Water	1	22	−1·52	−76·00	−338·3

Codeine Succinate, $(C_{18}H_{21}O_3N)_2,C_4H_6O_4$.

White needles, melting at 79—80°:

0·1346 gave 0·3307 CO_2 and 0·0787 H_2O. C = 67·01; H = 6·50.

$C_{40}H_{48}O_{10}N_2$ requires C = 67·04; H = 6·70 per cent.

Solvent.	Percentage concentration.	Temp.	α.	[α]D.	[M]D.
Chloroform	4	23°	−7·02	−87·75	−628·3
,, ...	2	23	3·50	87·50	626·5
,, ...	1	23	1·80	90·00	644·4
Water	1	25	−2·06	−103·00	−737·5

Codeine Maleate, $(C_{18}H_{21}O_3N)_2,C_4H_4O_4$.

Deliquescent, colourless crystals, becoming semi-liquid on exposure to air:

0·1192 gave 0·2944 CO_2 and 0·0706 H_2O. C = 67·35; H = 6·58.
$C_{40}H_{46}O_{10}N_2$ requires C = 67·22; H = 6·44 per cent.

Solvent.	Percentage concentration.	Temp.	α.	$[\alpha]_D$.	$[M]_D$.
Chloroform	4	22°	−6·46	−80·75	−576·6
,, ...	2	22	3·22	80·50	574·8
,, ...	1	22	1·60	80·00	571·2
Water	1	25	−1·86	−93·00	−664·0

Codeine Fumarate, $(C_{18}H_{21}O_3N)_2,C_4H_4O_4,4\frac{1}{2}H_2O$.

White, crystalline flakes, sparingly soluble in alcohol and water, melting when hydrated at 95°:

0·1804 gave 0·4004 CO_2 and 0·1210 H_2O. C = 60·52; H = 7·45.
$C_{40}H_{46}O_{10}N_2,4\frac{1}{2}H_2O$ requires C = 60·37; H = 6·92 per cent.

Solvent.	Percentage concentration.	Temp.	α.	$[\alpha]_D$.	$[M]_D$.
Chloroform	4	22°	−6·52	−81·50	−581·9
,, ...	2	22	3·25	81·25	580·1
,, ...	1	22	1·66	83·00	592·6
Water	1	22	−1·80	−90·00	−642·6

Codeine Acetylenedicarboxylate, $(C_{18}H_{21}O_3N)_2,C_4H_2O_4,6H_2O$.

White prisms, melting when hydrated at 68°:

0·1904 gave 0·4090 CO_2 and 0·1112 H_2O. C = 58·59; H = 6·49.
$C_{40}H_{44}O_{10}N_2,6H_2O$ requires C = 58·53; H = 6·83 per cent.

Solvent.	Percentage concentration.	Temp.	α.	$[\alpha]_D$.	$[M]_D$.
Chloroform	4	22°	−6·13	−76·62	−545·5
,, ...	2	22	2·95	73·75	525·1
,, ...	1	22	1·36	68·00	484·2
Water	1	22	−1·75	−87·50	−623·0

IV. *Cinchonine Salts.*

This alkaloid melted at 257° before, and at 253·5° after, use in the preparation of the salts required. Its rotatory power in alcohol solution was:

Percentage concentration.	Before use.				After use.			
	Temp.	α.	$[\alpha]_D$.	$[M]_D$.	Temp.	α.	$[\alpha]_D$.	$[M]_D$.
0·5	23°	+2·22	+222·0	+652·7	22°	+2·17	+217·0	+638·0

Cinchonine β-Phenylpropionate, $C_{19}H_{22}ON_2,(C_9H_{10}O_2)_2$.

This salt did not crystallise readily, but solidified to a horny mass:

0·1353 gave 0 3723 CO_2 and 0·0894 H_2O. C = 75·05; H = 7·34.

$C_{37}H_{42}O_5N_2$ requires C = 74·75; H = 7·07 per cent.

Solvent.	Percentage concentration.	Temp.	α.	$[\alpha]_D$.	$[M]_D$.
Chloroform	4	23°	+9·30	+116·25	+690·5
,, ...	2	23	4 82	120·50	715·7
,, ...	1	23	2·50	125·00	742·5
Water	0·5	23	+0·98	+98·00	+582·1

Cinchonine Cinnamate, $C_{19}H_{22}ON_2,(C_9H_8O_2)_2$.

Small, hard needles, melting at 129°:

0·1542 gave 0·4248 CO_2 and 0·0882 H_2O. C = 75·11; H = 6·35.

$C_{37}H_{38}O_5N_2$ requires C = 75·25; H = 6·44 per cent.

Solvent.	Percentage concentration.	Temp.	α.	$[\alpha]_D$.	$[M]_D$.
Chloroform	4	23°	+8·60	+107·50	+634·5
,, ...	2	23	4·34	108·50	640·3
,, ...	1	23	2·43	121·50	716·8
Water	0·5	23	+1·17	+117·00	+690·3

Cinchonine Phenylpropionate, $C_{19}H_{22}ON_2,(C_9H_6O_2)_2$.

This salt also resisted crystallisation and appeared as a horny mass:

0·1194 gave 0·3316 CO_2 and 0·0662 H_2O. C = 75·73; H = 6·16.

$C_{37}H_{34}O_5N_2$ requires C = 75·77; H = 5·80 per cent.

Solvent.	Percentage concentration.	Temp.	α.	$[\alpha]_D$.	$[M]_D$.
Chloroform	4	23°	+6·88	86·00	+504·0
,, ...	2	23	3·70	92·50	542·0
,, ...	1	23	2·00	100·00	586·0
Water	0·5	23	+0·92	+92·00	+539·1

Cinchonine Succinate, $C_{19}H_{22}ON_2,C_4H_6O_4,3\frac{1}{2}H_2O$.

White, feathery crystals, which commence to foam at 82—84° and melt to a clear liquid at 110°:

0·1324 gave 0·2830 CO_2 and 0·0872 H_2O. C = 58·28; H = 7·32.

$C_{23}H_{28}O_5N_2,3\frac{1}{2}H_2O$ requires C = 58·11; H = 7·36 per cent.

Solvent.	Percentage concentration.	Temp.	α.	$[\alpha]_D$.	$[M]_D$
Chloroform	4	22°	+12·72	+159·00	+655 1
,, ...	2	22	6·48	162·00	667·4
,, ...	1	22	3·31	165·50	681·9
Water	0·5	23	+1·40	+140·00	+576·8

Cinchonine Maleate, $C_{19}H_{22}ON_2,C_4H_4O_4,\frac{1}{2}H_2O$.

Small, compact crystals, charring at 144—146°:

0·1327 gave 0·3203 CO_2 and 0·0802 H_2O. C = 65·82; H = 6·71.
$C_{23}H_{26}O_5N_2,\frac{1}{2}H_2O$ requires C = 65·88; H = 6·46 per cent.

Solvent.	Percentage concentration.	Temp.	a.	[a]D.	[M]D.
Chloroform	4	22°	+9·42	+117·75	+482·8
,, ...	2	22	4·78	119·50	490·0
,, ...	1	22	2·50	125·00	512·5
Water	0·5	23	+1·43	+143·00	+586·3

Cinchonine Fumarate, $C_{19}H_{22}ON_2,C_4H_4O_4,2\frac{1}{2}H_2O$.

White, cubical crystals, melting indefinitely at 172—175°:

0·1140 gave 0·2548 CO_2 and 0·0745 H_2O. C = 60·98; H = 7·26.
$C_{23}H_{26}O_5N_2,2\frac{1}{2}H_2O$ requires C = 60·66; H = 6·82 per cent.

Solvent.	Percentage concentration.	Temp.	a.	[a]D.	[M]D.
Chloroform	4	22°	+11·65	+145·63	+597·1
,, ...	2	22	5·75	143·75	589·4
,, ...	1	22	2·80	140·00	574·0
Water	0·5	22	+1·39	+139·00	+569·9

Cinchonine Acetylenedicarboxylate, $C_{19}H_{22}ON_2,C_4H_2O_4,4H_2O$.

White tablets, darkening at 180—183°:

0·1073 gave 0·2282 CO_2 and 0·0660 H_2O. C = 57·99; H = 6·83.
$C_{23}H_{24}O_5N_2,4H_2O$ requires C = 57·50; H = 6·67 per cent.

Solvent.	Percentage concentration.	Temp.	a.	[a]D.	[M]D.
Chloroform	4	22°	+9·58	+119·75	+488·6
,, ...	2	22	5·08	127·00	518·2
,, ...	1	22	2·67	133·50	544·7
Water	0·5	22	+1·37	+137·00	+559·0

The nature of the above results is better shown by the following table, which gives the specific rotation of each alkaloid used, together with the specific rotations of each salt measured under similar conditions.

Salts of	Brucine.			Coniine.			Codeine.			Cinchonine.			
Approximate percentage concentrations	4.	2.	1.	4.	2.	1.	4.	2.	1.	4.	2.	1.	0·5.
Sp. rotation of free alkaloid.	−122·0	121·5	120·0	+8·00	8·50	9·00	−115·63	112·50	116·50	—	—	—	+222·0
β-Phenylpropionate	−38·19	38·46	38·46	−1·87	1·75	2·00	−64·37	64·25	63·35	+116·25	120·50	125·00	—
Cinnamate	−11·68	13·74	17·58	−7·50	7·50	8·50	−51·63	52·00	52·50	+107·50	108·50	121·50	—
Phenylpropiolate	+3·33	3·20	2·67	−7·12	6·75	7·00	−51·00	49·75	50·50	+ 86·00	92·50	100·00	—
Succinate	−68·75	73·25	75·50	+5·12	5·00	5·00	−87·75	87·50	90·00	+159·00	162·00	165·50	—
Maleate	—	−63·22	61·51	+4·38	4·75	4·50	−80·75	80·50	80·00	+117·75	119·50	125·00	—
Fumarate	—	−61·45	62·58	+4·00	4·25	4·50	−81·50	81·25	83·00	+145·63	143·75	140·00	—
Acetylenedicarboxylate	−61·67	70·06	70·06	+3·37	3·50	4·00	−76·62	73·75	68·00	+119·75	127·00	133·50	—
Hydrogen succinate	—	—	−23·40	—			—			—			
,, maleate..............	—	—	+6·11										
,, fumarate	—	—	+10·69										
,, acetylenedicarb-oxylate	—	—	−5·36										

It is thus readily seen that the unsaturated acids have invariably a greater effect than the saturated acids on the specific rotation of the combined alkaloid, but the effect caused by the presence of an acetylenic linking is not the same for all types of base or acid, and it appears that the change of rotatory power is dependent on the constitution of both constituents of the salt molecule as well as on the simple change of constitution due to increasing unsaturation. It was shown in Part 1 of this series (*loc. cit.*) that, in the case of such compounds as these, the change of rotation is to be considered relatively to the original rotatory power of the optically active part of the molecule, and in the following table the different types of esters and salts examined are enumerated, together with the relative effect ("least," "intermediate," "greatest") on the optical activity of the alcohol or base caused by each degree of unsaturation:

	Saturated.	Ethylenic.	Acetylenic.
Amyl esters of the cinnamic, &c., series (Walden, *Zeitsch. physikal. Chem.*, 1896, **20**, 569)	Least	Greatest	Intermediate
Coniine salts of the cinnamic, &c., series ...	,,	,,	,,
Brucine ,, ,, succinic, &c., ,, ...	,,	,,	,,
Brucine, codeine, and cinchonine salts of the cinnamic, &c., series	Least	Intermediate	Greatest
Coniine, codeine, and cinchonine salts of the succinic, &c., series	,,	,,	,,
Menthyl and bornyl esters of the cinnamic, &c., series (Part I, *loc. cit.*).................	Intermediate	Greatest	Least.

Several interesting conclusions may be drawn from this and the preceding table; in the first place, the salts of cinnamic and phenylpropiolic acids have specific rotations more widely removed from those of the alkaloids concerned than those of the salts of any of the other acids. The masses of the acids do not vary greatly, and the change of constitution is of exactly the same order as in the case of the aliphatic acids, and the only apparent cause of the very large optical effect produced is that in both these acids there exist essentially two unsaturated groups in close proximity to one another, and to the optically active part of the molecule. Further experiments are in progress with the object of investigating this point, and, meanwhile, it is noteworthy that Walden (*loc. cit.*) obtained a similar effect with these two acids in the case of the amyl esters.

Besides the differences thus disclosed between the effects of different types of acids, there also exist well-marked differences depending on the basic part of the molecule. The order of effect of unsaturation for amyl esters of the cinnamic series of acids (Walden) and for coniine salts of the same series is the same, but differs from that observed in the case of brucine, codeine, and cinchonic salts. It is, of course, impossible to state the precise configuration of the latter alkaloids, but all three differ from coniine in being exceedingly complicated, whereas this compound is a simple saturated substance, containing only one asymmetric carbon atom; thus being more nearly comparable with amyl alcohol. The series of amyl esters of the succinic series of acids is incomplete, but it is proposed to prepare the esters of these acids with another simple optically active alcohol in order to see if the effect of unsaturation is the same in this case as with coniine.

Lastly, the menthyl and bornyl compounds stand in an entirely different order from any of the others, and it is significant that these are derived from alcohols possessing a complicated stereochemical configuration, which, although precisely the same in both cases, is certain not to occur in any of the substances now investigated.

With regard to the relative effect of maleic and fumaric acids, the values obtained in the present work, taken in conjunction with the previous investigations of Hartwall and of Walden (*loc. cit.*), tend to show that here, also, no simple rule holds, for different results have been obtained with the various bases used.

The values of the molecular rotation of the salts in dilute aqueous solution lie almost without exception between that of the "alkaloid ion" (determined from the results obtained for salts, such as hydrochlorides, by previous workers) and that of the alkaloid itself. It may therefore be said that the Oudemans-Landolt law is valid in all the cases observed, for, since the acids used are comparatively weak, hydrolysis of the salts and also incomplete dissociation into the constituent ions would be anticipated, and either of these conditions would, in general, give values for the optical rotatory power lying closer to that of the alkaloid itself than that of its ion; indeed, it is noticeable that the values for the stronger acids approach more nearly to those for the ions to which reference has been made.

The conclusions drawn from this part of the work may be summarised as follows:

(1) The change in rotatory power of corresponding optically active saturated ethylenic and acetylenic compounds does not lie always in the same direction, but depends on the structure and configuration of the asymmetric part of the molecule, and, to a less extent, on the constitution of the rest of the molecule.

(2) Series of similarly constituted substances, however, usually show change of activity in the same direction, and in all cases the ethylenic compound possesses greater rotatory effect than the saturated compound.

(3) Similarly, no definite rule can be given for the relative effect on optical rotatory power of the maleinoid and fumaroid forms of *cis*- and *trans*-stereoisomeric compounds; this agrees with Hartwall's observations (*loc. cit.*).

(4) The Oudemans-Landolt law is probably correct in the case of alkaloid salts of weak acids, allowance being made for the effect due to hydrolysis and incomplete dissociation.

The author's best thanks are due to Prof. Collie, Dr. Smiles, and Dr. Stewart for continued interest and advice.

THE ORGANIC CHEMISTRY LABORATORY,
UNIVERSITY COLLEGE,
LONDON.

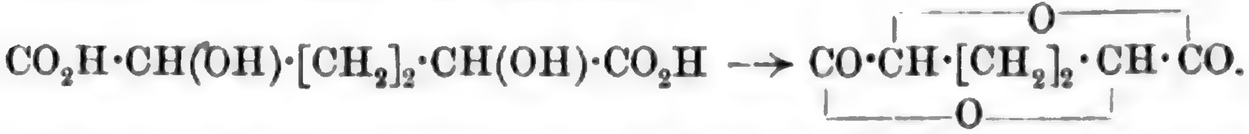
LXVI.—*The Action of Heat on α-Hydroxycarboxylic Acids. Part IV. Racemic αα′-Dihydroxyadipic Acid and meso-αα′-Dihydroxyadipic Acid.*

By HENRY RONDEL LE SUEUR.

THE results of the investigation of the action of heat on several α-monohydroxymonocarboxylic acids and on one αα′-dihydroxy-derivative of a dicarboxylic acid (sebacic acid) have been already communicated to the Society (Trans., 1904, **85**, 827; 1905, **87**, 1888; 1907, **91**, 1365).

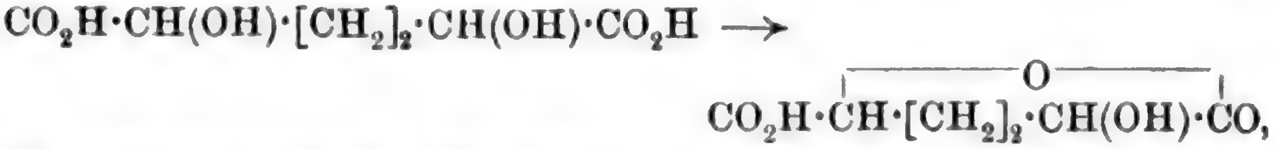
Sebacic acid was, until recent years, the only higher member of the oxalic acid series available in large quantities, but the fact that *cyclo*hexanone can now be purchased at a reasonable price, and that it yields adipic acid on oxidation with potassium permanganate, has enabled the work to be extended to α-hydroxy-derivatives of this acid.

The dibromoadipic acid, obtained by the action of bromine on the acid chloride, was readily converted into the corresponding hydroxy-derivatives by boiling an aqueous solution of its sodium salt. On attempting to purify the resulting product, it was soon recognised that it was not a homogeneous substance, but consisted of two hydroxy-acids, which were eventually obtained in a pure state by fractional extraction with acetone and repeated crystallisation from a mixture of acetone and chloroform. One of these αα′-dihydroxyadipic acids melts at 146°, and when heated readily loses water and gives a beautifully crystalline sublimate of its dilactone:



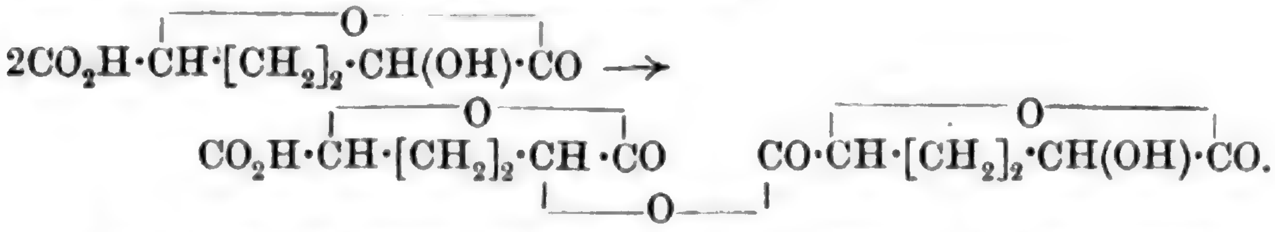
$$CO_2H\cdot CH(OH)\cdot[CH_2]_2\cdot CH(OH)\cdot CO_2H \longrightarrow \overbrace{CO\cdot \underbrace{CH\cdot[CH_2]_2\cdot CH}_{O}\cdot CO}^{O}.$$

The other αα′-dihydroxyadipic acid melts at 174°, and when heated loses water, but no trace of a sublimate is formed, and the resulting product consists of the lactone-lactide of the acid. This compound may be regarded as resulting from two distinct decompositions: first, the formation of a lactonic acid,



$$\mathrm{CO_2H\cdot CH(OH)\cdot[CH_2]_2\cdot CH(OH)\cdot CO_2H} \longrightarrow \mathrm{CO_2H\cdot\overbrace{CH\cdot[CH_2]_2\cdot CH(OH)\cdot CO}^{O}},$$

and then the union of two molecules of this substance, with loss of water and formation of a lactone-lactide:



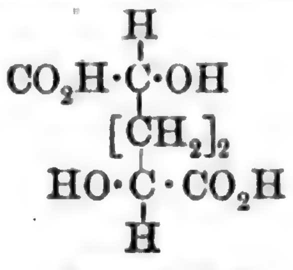
$$\mathrm{2CO_2H\cdot\overbrace{CH\cdot[CH_2]_2\cdot CH(OH)\cdot CO}^{O}} \longrightarrow \mathrm{CO_2H\cdot\overbrace{CH\cdot[CH_2]_2\cdot CH\cdot CO}^{O}}\underbrace{\quad\qquad}_{O}\mathrm{CO\cdot\overbrace{CH\cdot[CH_2]_2\cdot CH(OH)\cdot CO}^{O}}.$$

In the previous communications (*loc. cit.*) relating to this investigation, it was shown that a-monohydroxy-acids, of which the above lactonic acid may be regarded as an example, readily form lactides when heated at about 200°.

Since aa′-dihydroxyadipic acid contains two asymmetric carbon atoms, the existence of a racemic and meso-variety was to be expected. The fact that totally different products are obtained on heating the two acids, led to a closer examination of the space formulæ of these substances.

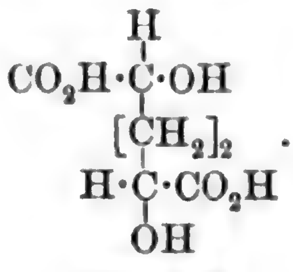
If we consider the space formula of a racemic aa′-dihydroxyadipic acid, it will be seen that if one of the hydroxyl groups is directly above the carboxyl group with which it will form a lactone, then the other hydroxyl group will be directly below the other carboxyl group, and consequently a dilactone will be quite as easily formed as a monolactone.

A similar consideration of the space formula of a meso-aa′-dihydroxyadipic acid leads to a totally different result. In this case, if one of the hydroxyl groups be directly above the carboxyl group with which it will form a lactone, then the other hydroxyl group is not directly under a carboxyl group, but under a hydrogen atom. It will therefore be readily admitted that, whereas a monolactone can be formed easily from the meso-acid, the formation of a dilactone, if not an impossibility, is, at all events, very highly improbable:



$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{CO_2H\cdot C\cdot OH} \\ | \\ \mathrm{[CH_2]_2} \\ | \\ \mathrm{HO\cdot C\cdot CO_2H} \\ | \\ \mathrm{H} \end{array}$$

Racemic Acid.



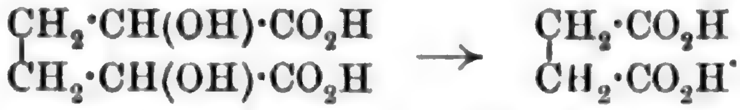
$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{CO_2H\cdot C\cdot OH} \\ | \\ \mathrm{[CH_2]_2} \\ | \\ \mathrm{H\cdot C\cdot CO_2H} \\ | \\ \mathrm{OH} \end{array}$$

meso-Acid.

Although the two CH_2 groups have not been taken into consideration, this in no way affects the validity of the above deductions, in fact, the presence of these groups only renders the formation of a dilactone from the meso-acid all the more improbable.

If the above arguments be correct, then the acid melting at 146° and which easily forms a dilactone must be the racemic variety, and the acid which melts at 174° and yields a lactone-lactide but not a dilactone is the meso-acid. In order definitely to settle this point, both acids were submitted to the alkaloid method of resolving optically inactive compounds containing asymmetric carbon atoms, and the results obtained are in complete agreement with, and fully justify, the above conclusions. By fractional crystallisation of the cinchonidine salt of the acid melting at 146°, it was resolved into its *d*- and *l*-forms, whereas a similar treatment of the meso-acid failed to produce any trace of an optically active acid. In connexion with this resolution, it is interesting to note that the ammonium salt of the *d*-acid is strongly lævorotatory.

That the hydroxyl groups in both acids are attached to *d*-carbon atoms and not to β- or γ-atoms is conclusively proved by the fact that both acids yield succinic acid when they are oxidised with potassium permanganate:



$$\begin{array}{l} CH_2\cdot CH(OH)\cdot CO_2H \\ CH_2\cdot CH(OH)\cdot CO_2H \end{array} \longrightarrow \begin{array}{l} CH_2\cdot CO_2H \\ CH_2\cdot CO_2H \end{array}.$$

Rosenlew (*Ber.*, 1904, **37**, 2092) obtained two $\alpha\alpha'$-dihydroxyadipic acids, one melting at 173° and the other at 132—134°, and concluded from the melting points and the relative solubilities of these acids that the first was the racemic acid and the second the meso-variety. The results now described show that Rosenlew's deductions are not correct, and that his acid melting at 173° corresponds with the meso-acid (m. p. 174°) mentioned in this paper, and the acid which he describes as melting at 132—134° is undoubtedly the impure racemic acid.

EXPERIMENTAL.

Preparation of $\alpha\alpha'$-Dibromoadipic Acid.

One hundred and fifteen grams of adipic acid (m. p. 148·5—150°), obtained by the oxidation of *cyclo*hexanone with potassium permanganate in alkaline solution, were converted into the acid chloride by the action of phosphorus pentachloride; 280 grams of dry bromine were gradually added to the resulting acid chloride, and the mixture heated on the water-bath until the whole of the bromine had disappeared. The resulting liquid bromo-acid chloride was gradually poured into 450 c.c. of formic acid (sp. gr. 1·20), and, when the somewhat violent reaction had subsided, the product was heated on the water-bath for half an hour; on cooling, 234 grams (theory, 239 grams) of the dibromo-acid, melting at 180—182°, crystallised out. A small quantity was recrystallised from formic acid (sp. gr. 1·22) until its melting point was constant, when it was obtained in prismatic needles melting at 192—193°, a melting point which agrees with that of one of the dibromoadipic acids prepared by Rosenlew (*Ber.*, 1904, **37**, 2091):

0·1618 gave 0·2016 AgBr. Br = 53·0.

$C_6H_8O_4Br_2$ requires Br = 52·6 per cent.

Preparation of Racemic aa'-Dihydroxyadipic Acid and meso-aa'-Dihydroxyadipic Acid.

One hundred and nineteen grams of dibromoadipic acid (m. p. 180—182°) were added to 600 c.c. of water, neutralised with sodium hydroxide, and the resulting solution boiled under a reflux apparatus for three hours, at the end of which time the solution was strongly acid. It was again neutralised with sodium hydroxide and boiled for a further three hours. If at the end of this second period the solution is still neutral, this indicates that the reaction is completed, otherwise it must be neutralised again and boiled for three hours more. The hot solution of the sodium salt was added to an excess of a hot solution of copper sulphate, and the whole allowed to remain overnight, when the copper salt gradually separated in a crystalline form; it was filtered, washed free from sodium bromide, and decomposed with hydrogen sulphide. The filtrate obtained after removal of the copper sulphide was evaporated to dryness on the water-bath, powdered, and thoroughly dried over sulphuric acid in a vacuum.

The two isomeric *aa'*-dihydroxyadipic acids which constitute the residue were separated as follows: 82 grams of the finely-powdered and dried residue were boiled with 250 c.c. of acetone and filtered, and this process repeated five times, using 250 c.c. of acetone for each extraction. The undissolved residue (A), which melted at 165—166° and weighed 13 grams, consisted for the most part of the meso-acid (see p. 722).

The several filtrates were allowed to cool, and the six fractions which separated were filtered and their melting points determined. The filtrates obtained from these were concentrated to a small bulk, and another series of fractions obtained. These fractions, which melted at the same temperature, were mixed together and recrystallised from a mixture of acetone and chloroform until the melting point was constant, when the acid was obtained in aggregates of small plates melting at 146° (compare Rosenlew, *loc. cit.*):

0·1372 gave 0·2020 CO_2 and 0·0718 H_2O. C = 40·15; H = 5·81.

$C_6H_{10}O_6$ requires C = 40·45; H = 5·62 per cent.

r-*aa'-Dihydroxyadipic acid* is very soluble in water or alcohol, sparingly so in boiling acetone, and insoluble in ether, chloroform, light petroleum, or benzene. When heated, it loses water and the corresponding dilactone is formed. The molecular weight was determined by titration with *N*/10 sodium hydroxide, using phenolphthalein as indicator:

0·1812 required 20·16 c.c. *N*/10 NaOH. M.W. = 179·6.

A dibasic acid, $C_6H_{10}O_6$, requires M.W. = 178.

The *silver* salt was prepared by adding a hot solution of the ammonium salt to a hot solution of silver nitrate, when, on remaining for some time, a crystalline precipitate was obtained:

0·2084 gave 0·1142 Ag. Ag = 54·80.

$C_6H_8O_6Ag_2$ requires Ag = 55·10 per cent.

r-*aa'-Dihydroxyadipamide*,

$CO{\cdot}NH_2{\cdot}CH(OH){\cdot}[CH_2]_2{\cdot}CH(OH){\cdot}CO{\cdot}NH_2$,

was prepared by heating the dilactone with a saturated alcoholic solution of ammonia in a sealed tube at 120° for eight hours. The crystalline solid which separated out on cooling was crystallised from 92 per cent. alcohol, when it was obtained in small, glistening plates melting with effervescence at 177°. It readily dissolves in cold water, is sparingly soluble in boiling alcohol, and insoluble in ether, light petroleum, acetone, or chloroform:

0·1264 gave 17·2 c.c. moist nitrogen at 15° and 760 mm. N = 15·93.

$C_6H_{12}O_4N_2$ requires N = 15·90 per cent.

r-*aa'-Dihydroxyadipic dianilide*,

$C_6H_5{\cdot}NH{\cdot}CO{\cdot}CH(ON){\cdot}[CH_2]_2{\cdot}CH(OH){\cdot}CO{\cdot}NH{\cdot}C_6H_5$,

was prepared by boiling 2 grams of the acid with 6 grams of recently distilled aniline for seven hours. The resulting product was treated with dilute hydrochloric acid to remove excess of aniline, and the solid crystallised from alcohol, when it was obtained in glistening plates melting at 186°. It is insoluble in ether, benzene, chloroform, or light petroleum, and moderately soluble in boiling acetone or alcohol:

0·1394 gave 0·3342 CO_2 and 0·0768 H_2O. C = 65·39; H = 6·12.
0·1604 „ 12·35 c.c. moist nitrogen at 15° and 757 mm. N = 8·97.

$C_{18}H_{20}O_4N_2$ requires C = 65·85; H = 6·10; N = 8·53 per cent.

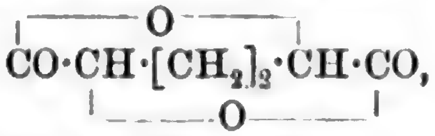
Action of Heat on Racemic aa'-Dihydroxyadipic Acid.

The acid was placed in a small retort connected to a receiver, and the latter connected to a water-pump. The pressure was reduced to 25—30 mm., and the retort and contents heated at 160—170° in an air-bath, a slow current of dry air being passed through the apparatus. As soon as the substance had melted, water was evolved, and a crystalline sublimate collected in the neck of the retort; it was resublimed and analysed:

0·1246 gave 0·2300 CO_2 and 0·0530 H_2O. C = 50·34; H = 4·72.

$C_6H_6O_4$ requires C = 50·70; H = 4·23 per cent.

The *dilactone* of *r*-αα′-dihydroxyadipic acid,



$$CO\cdot CH\cdot[CH_2]_2\cdot CH\cdot CO,$$

melts at 134°, is insoluble in light petroleum, alcohol, or water in the cold, readily soluble in cold acetone and in boiling alcohol, from which it crystallises in well-defined plates on cooling. The dilactone is insoluble in water, but on remaining in contact with this liquid it is gradually hydrolysed to the parent acid, which dissolves in the water, giving a strongly acid solution. That this solution contains the parent acid was shown by analysis of the silver salt prepared from it:

0·1542 gave 0·0850 Ag. Ag = 55·12.

$C_6H_8O_6Ag_2$ requires Ag = 55·10 per cent.

Resolution of Racemic αα′-Dihydroxyadipic Acid.

Preliminary experiments with quinine, cinchonine, and cinchonidine showed that only the last of these alkaloids is suitable for this resolution. The following is the method adopted: 29 grams (1 mol.) of the *r*-acid were dissolved in 450 c.c. of water and 50 grams (1 mol.) of cinchonidine added; these readily dissolved on warming. The resulting strongly acid solution was allowed to remain overnight, when 33 grams of a beautifully crystalline, neutral cinchonidine salt were deposited; this was filtered and recrystallised from water until the optical activity was not increased by further recrystallisation. This was ascertained by dissolving 1 gram of the salt in water, precipitating the alkaloid by ammonia, filtering, and evaporating the filtrate to a few c.c. This solution had now a faintly acid reaction, so it was again made faintly alkaline with ammonia, allowed to remain for some time, and the small amount of alkaloid which had separated was filtered, washed with a little water, and the filtrate made up to the volume required to fill the 2·2-dcm. tube, in which it was examined. All these experiments were carried out under identical conditions, in order that the results might be truly comparable.

The pure *l*-base *d*-acid salt, which weighed 16 grams, was dissolved in water, the alkaloid precipitated with ammonia, and the resulting ammonium salt converted into the copper salt, which was filtered and decomposed with hydrogen sulphide. The filtrate from the copper sulphide was evaporated on the water-bath, the residue dried in a vacuum, and then crystallised from a mixture of acetone and chloroform until its melting point was constant.

d-αα'-Dihydroxyadipic acid is insoluble in ether or light petroleum, readily soluble in water, moderately so in alcohol or acetone, and crystallises from a mixture of acetone and chloroform in long, slender needles melting at 157° with effervescence.

A determination of the specific rotation gave the following result:

0·9866, made up to 16 c.c. in a 2·2-dcm. tube, gave α^{16} $+0·52°$, whence $[\alpha]_D^{16}$ $+3·8°$.

The above solution was carefully neutralised with ammonia and made up to 20 c.c., and on examination was found to have an opposite rotation to that of the free acid, and gave α^{11} $-2·77°$, whence $[\alpha]_D^{11}$ $-21·4°$.

Attempts were made to isolate the pure *l*-acid from the mother liquors from which the *d*-acid had been separated, but the amount of material was not sufficient to admit of the isolation of a pure specimen of the *l*-isomeride.

Oxidation of Racemic αα'-Dihydroxyadipic Acid.

One gram of the acid was dissolved in 20 c.c. of water, and to this a hot solution of 2·5 grams of potassium permanganate in 50 c.c. of water was gradually added. A vigorous oxidation took place, and, when all the potassium permanganate had been reduced, the manganese dioxide was filtered and the filtrate evaporated to dryness. The residue, when heated with resorcinol and a few drops of sulphuric acid and pouring into a solution of potassium hydroxide, gave a very marked fluorescein reaction. No attempt was made to isolate the succinic acid itself, and so the residue was boiled with excess of acetyl chloride for two hours, the excess of acetyl chloride evaporated, and the dried residue extracted with benzene. One gram of aniline was added to the benzene solution, and, after a short time, a crystalline solid separated out, which, after crystallisation from water, was obtained in aggregates of flat needles melting at 148° (succinanilic acid melts at 148·5°). The corresponding anil was obtained by boiling the anilic acid for a short time and crystallising the resulting product from alcohol, when it was obtained in long, slender needles melting at 153—154°.

meso-αα'-Dihydroxyadipic Acid.

The insoluble residue A (see p. 719), left after repeated extraction of the mixed acids with acetone, was crystallised from a mixture of alcohol and chloroform until its melting point was constant:

0·1524 gave 0·2254 CO_2 and 0·0804 H_2O. C = 40·33; H = 5·86.

$C_6H_{10}O_6$ requires C = 40·45; H = 5·62 per cent.

meso-aa′-Dihydroxyadipic acid is insoluble in ether or light petroleum, only slightly soluble in chloroform, acetone, or alcohol in the cold, and readily so in water or in boiling alcohol, from which it crystallises in small, glistening plates melting at 174°. This acid is considerably less soluble in alcohol than its racemic isomeride.

Attempts were made to resolve this acid by means of its cinchonidine salt, but no evidence whatever of the production of an optically active acid was obtained.

A mixture of equal parts of the above acid and the racemic isomeride contracts at 146° and melts at 161—165°.

The molecular weight was determined by titration with sodium hydroxide, using phenolphthalein as indicator:

0·1672 required 18·65 c.c. *N*/10 NaOH. M.W. = 179·2.

A dibasic acid, $C_6H_{10}O_6$, requires M.W. = 178.

The *silver* salt was prepared by adding a solution of the ammonium salt of the acid to a solution of silver nitrate. The crystalline salt was deposited more quickly than the corresponding salt of the racemic acid:

0·2076 gave 0·1142 Ag. Ag = 55·01.

$C_6H_8O_6Ag_2$ requires Ag = 55·10 per cent.

Oxidation with Potassium Permanganate.—The oxidation was carried out exactly as described for the oxidation of the racemic isomeride. The product of oxidation gave the fluorescein reaction, and from it both succinanilic acid, melting at 148°, and succinanil, melting at 153—154°, were prepared.

Methyl meso-aa′-dihydroxyadipate,

$CO_2Me{\cdot}CH(OH){\cdot}[CH_2]_2{\cdot}CH(OH){\cdot}CO_2Me$,

was prepared by adding 12 grams of methyl iodide to 10 grams of the dry silver salt, suspended in dry benzene, and heating on the water-bath for three hours. The silver iodide was filtered and the filtrate evaporated, when the ester was obtained as a crystalline solid, which, after crystallisation from a mixture of benzene and light petroleum, was obtained in stout needles melting at 89°. It is somewhat readily soluble in cold acetone, alcohol, or water, and sparingly so in cold benzene or chloroform:

0·1520 gave 0·2568 CO_2 and 0·0956 H_2O. C = 46·10; H = 7·00.

$C_8H_{14}O_6$ requires C = 46·60; H = 6·80 per cent.

meso-aa′-Dihydroxyadipamide,

$CO{\cdot}NH_2{\cdot}CH(OH){\cdot}[CH_2]_2{\cdot}CH(OH){\cdot}CO{\cdot}NH_2$,

was obtained by the following two methods: (I) the lactone-lactide, obtained by heating the meso-acid, was boiled with a concentrated solution (sp. gr. 0·880) of ammonia, the solution filtered, and allowed to remain, when the diamide separated out; (2) the dimethyl ester was added to a concentrated solution (sp. gr. 0·880) of ammonia, in which it readily dissolved, and from this solution the diamide soon separated. It was crystallised from water, and obtained in glistening plates melting and decomposing at 242°. It dissolves somewhat readily in boiling water, and is insoluble in all the ordinary organic solvents:

0·1462 gave 19·7 c.c. moist nitrogen at 15° and 763 mm. N = 15·84.
$C_6H_{12}O_4N_2$ requires N = 15·90 per cent.

meso-αα'-Dihydroxyadipic dianilide,

$$C_6H_5\cdot NH\cdot CO\cdot CH(OH)\cdot[CH_2]_2\cdot CH(OH)\cdot CO\cdot NH\cdot C_6H_5,$$

was prepared in exactly the same way as the dianilide of the racemic acid. It is insoluble in water, ether, chloroform, benzene, or light petroleum, and moderately soluble in alcohol, from which it crystallises in glistening plates melting at 216°:

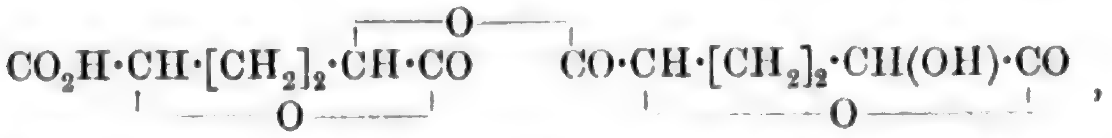
0·1526 gave 11·2 c.c. moist nitrogen at 15° and 775 mm. N = 8·76.
$C_{18}H_{20}O_4N_2$ requires N = 8·53 per cent.

Action of Heat on meso-αα'-Dihydroxyadipic Acid.

The acid was placed in a large test-tube fitted with a cork through which two tubes passed, the first of these was connected to a pump, and the second, which was drawn out to a fine point, served for the admission of a slow current of dry air. The test-tube and contents were gradually heated in an air-bath. At 174°, the substance melted and water-vapour was evolved, and the temperature was kept at 180—190° for about five minutes, the pressure being maintained at 35—40 mm. No sublimate was formed. The residue consisted of a hard, glassy substance, which gave the following results on analysis:

0·1552 gave 0·2710 CO_2 and 0·0670 H_2O. C = 47·62; H = 4·80.
$C_{12}H_{14}O_9$ requires C = 47·68; H = 4·63 per cent.

The *lactone-lactide* of meso-αα'-dihydroxyadipic acid,



$$CO_2H\cdot CH\cdot[CH_2]_2\cdot CH\cdot CO \qquad CO\cdot CH\cdot[CH_2]_2\cdot CH(OH)\cdot CO,$$

is a hard, transparent, glassy substance, which does not melt at 250°, and when heated above this temperature it decomposes without previously melting. It is insoluble in water, alcohol, acetone, chloroform, ether, or benzene, and dissolves in a solution of potassium hydroxide. When boiled with a concentrated solution of ammonia, the diamide (see p. 723) and the ammonium salt of the dihydroxy-acid are produced. The formation of the latter compound was proved by converting it into the corresponding silver salt, which was analysed:

0·1234 gave 0·0680 Ag. Ag = 55·10.

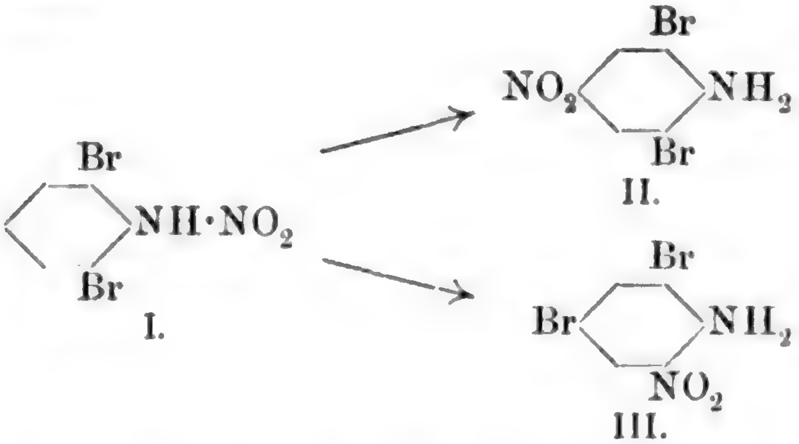
$C_6H_8O_6Ag_2$ requires Ag = 55·10 per cent.

Chemical Laboratory,
St. Thomas's Hospital,
London, S.E.

LXVII.—*The Wandering of Bromine in the Transformation of Nitroaminobromobenzenes.*

By Kennedy Joseph Previté Orton and Constance Pearson.

In the course of a series of experiments on the transformation of substituted bromo- and chloro-nitroaminobenzenes, we have observed a remarkable wandering of a bromine atom in the case of 2:6-dibromo-1-nitroaminobenzene (I). Under all conditions which are favourable to transformation, not only is the expected 2:6-dibromo-4-nitroaniline (II) produced, but also the isomeric 2:4-dibromo-6-nitroaniline (III), thus:



Although the position para with respect to the amino-group is unoccupied, the migrating nitro-group in part displaces an ortho-bromine atom, which then re-enters the benzene nucleus in the vacant para-position, the two nitroanilines being formed in about equal proportions.

The transformation of this di-*o*-substituted nitroaminobenzene is a far slower process than that of the nitroaminobenzenes with an ortho-position unoccupied; only in strongly acid solutions (8—9*N*) is the change complete in twenty-four hours. Inasmuch as the low solubility (1 part in 1400 parts) renders the use of water as a solvent impracticable, aqueous alcohol or acetic acid, 25 or 50 per cent., was employed.

Solutions of the nitroamine in all media can apparently be kept indefinitely. Change only occurs when acid is present. With low concentrations of acid, the rate of change is very slow, but becomes more rapid as the concentration is raised, until, when the acid is 8—9*N*, the change is complete in twenty-four hours at the ordinary temperature. For example, a solution of the nitroamine in which the acid was at a concentration of 2*N*, showed no signs of change in forty-eight hours, but contained nitroaniline after seventy-two hours. Neither variation in the concentration of the acid or of the nitroamine had any effect on the relative quantities of the two nitroanilines, or on the course of the transformation, but with dilute solutions, 0·75—1·5 grams in 100 c.c. of the solvent, the separation of the two anilines was simplified. Of the common strong acids, hydrochloric acid is the most effective in producing the rearrangement. As a weaker acid, sulphuric acid at equivalent concentrations does not accelerate the change so greatly as hydrochloric acid, whilst, in the presence of the stronger nitric and hydrobromic acids, reduction of nitroamine is the main reaction.

Comparative experiments were made with the isomeric 2 : 4-dibromo-1-nitroaminobenzene, in which one ortho- instead of the para-position is vacant. No wandering of a bromine atom was discernible, 2 : 4-dibromo-6-nitroaniline being the sole product.

The behaviour of *s*-tribromo-1-nitroaminobenzene, under similar treatment, was also examined, and was found to be surprisingly similar to that of the 2 : 6-dibromo-compound, with this one difference. Whereas in the case of the 2 : 6-dibromonitroaminobenzene, notwithstanding that the para-position is vacant, partial *displacement* of an ortho-placed bromine takes place, the bromine again entering the nucleus, transformation of the *s*-tribromonitroamine into a nitroaniline can only occur with *replacement* of bromine, which appears in the solution.* The nitroamine was transformed into a mixture of 2 : 4-dibromo-6-nitro- and 2 : 6-dibromo-4-nitro-anilines, which are present in approximately the same proportion as that obtained from the 2 : 6-dibromonitroamine. The change appeared somewhat slower with the *s*-tribromo-derivative for the lower concentrations of hydrochloric acid, but in both cases at a concentration of 8—9*N* no nitroamine remained after twenty-four hours.

---

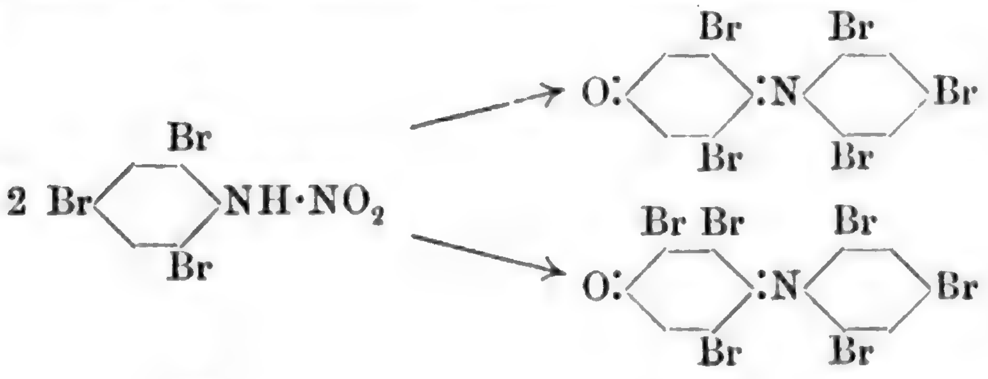
* The displacement of bromine in the para-position by the nitro-group (and formation of *s*-tribromonitroaminobenzene) in the action of nitric acid on *s*-tribromoaniline has already been described by one of us (Trans., 1902, **81**, 490). In the same communication, the references in the literature to similar displacements in *s*-trisubstituted bromoanilines and phenols are collected.

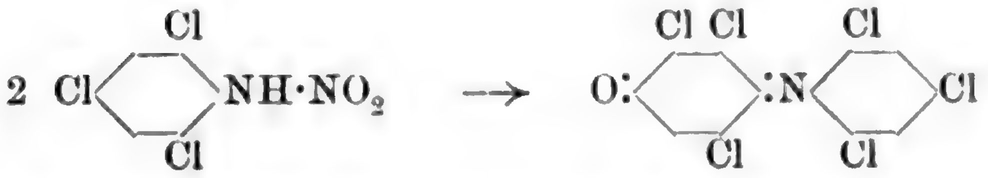
A great contrast is offered by the behaviour of *s*-trichloronitroamine. No nitroaniline is formed, that is, no replacement of chlorine by the nitro-group occurs. The characteristic product is chloroanil (tetrachlorobenzoquinone), trichloroaniline being formed at the same time. Under similar conditions as to solvent and concentration of acid, this reaction does not take place so rapidly as the transformation of the di- and tri-bromonitroamines. The formation of *s*-trichloroaniline points to hydrolysis of the nitroaminobenzene as one of the steps in the change:

$$C_6H_2Cl_3{\cdot}NH{\cdot}NO_2 + H_2O = C_6H_2Cl_3{\cdot}NH_2 + HNO_3.$$

It may be supposed that the chlorine arising from the interaction of the nitric and hydrochloric acids converts some of the *s*-trichloroaniline into tetrachlorobenzoquinone. Similar hydrolysis might be expected as a side reaction in the transformation of the bromonitroamines; the presence of very small quantities of bases in the mother liquors from the nitroaniline indicated that such occurred.

Under the conditions here described, no traces of the quinoneanils (phenyliminoquinones), recorded by one of us and Miss Smith (Trans., 1905, **87**, 309; *ibid.*, 1907, **91**, 146), were formed. In the production of these compounds, which arise in the action of sulphuric acid on the nitroamines in acetic acid solution, there is both replacement of halogen (in the case of *s*-tribromonitroaminobenzene) and migration of halogen from one carbon atom to another of the benzene nucleus, in the manner shown by the following constitutional formulæ:





How far the reactions recorded in this paper are analogous to these transformations cannot at present be decided, but the fact that 2:6-dibromonitroaminobenzene, in which the migration of bromine is observed during the conversion into nitroanilines, yields no quinoneanil, but mainly 2:6-dibromo-4-nitroaniline, when treated with sulphuric acid in acetic acid solution (*loc. cit.*) suggests some considerable difference.

The nitroanilines, although the main, are not the sole products of the transformation of the nitroamines in dilute alcoholic or acetic acid solution in the presence of hydrochloric or sulphuric acids. In all cases, reduction of a small amount of the nitroamine to diazo-compound takes place: $Ar{\cdot}NH{\cdot}NO_2 \longrightarrow (Ar{\cdot}N_2)^{\cdot}$. With other acids, nitric and hydrobromic, this production of diazo-compound assumes much larger proportions. In the case of *s*-trichloronitroaminobenzene, the reduction is quantitative, bromine being liberated when hydrobromic acid is used:

$$C_6H_2Cl_3{\cdot}NH{\cdot}NO_2 + 2HBr \longrightarrow (C_6H_2Cl_3{\cdot}N_2)^{\cdot} + H_2O + Br_2.$$

Hydrobromic acid and the *s*-tribromo-derivative yield the very sparingly soluble diazonium perbromide, $C_6H_2Br_3{\cdot}N_2{\cdot}Br_3$. At the same time, a small amount of the two nitrobromoanilines, the main products of the reaction with hydrochloric acid, can be isolated. When, however, nitric acid is used, although reduction is still the main reaction, replacement of the bromine by the nitro-group assumes larger proportions.

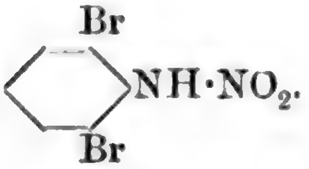
With 2:6-dibromonitroaminobenzene, the reaction with hydrobromic acid is more complicated, for the bromine set free in the reduction of the hydrobromic acid converts unchanged dibromonitroamine into *s*-tribromonitroamine, which in its turn is reduced to diazo-compound. Besides the reduction and bromination, the migration of the nitro-group also takes place, and to a larger extent than is the case with *s*-tribromonitroamine under the same conditions, both the dibromonitroanilines being easily isolated and separated.

It would be premature to attempt to account for the varying behaviour of these nitroamines, or for the part played by the hydrochloric (or sulphuric) acid. Although the union of the acid with the nitroamine as a preliminary step in the changes appears an attractive view, little experimental evidence can at present be brought forward in its favour.

Attention may be drawn to the marked effect of symmetry of the benzene nucleus in determining the point of attachment of the migrating nitro-group. Comparison of 2:6-dibromo- with 2:4-dibromo-nitroamines illustrates this fact clearly. In the symmetrical 2:6-dibromo-derivative, the nitro-group migrates both to the ortho- and para-positions, whereas in the 2:4-dibromonitroamine the wandering is exclusively to the ortho-position.

EXPERIMENTAL.

Transformation of 2 : 6-*Dibromo*-1-*nitroaminobenzene*,



2 : 6-Dibromo-1-nitroaminobenzene can readily be prepared in large quantity by the method previously described from 2 : 6-dibromoaniline (Orton, Trans., 1902, **81**, 808; Orton and Smith, Trans., 1905, **87**, 397). The solubilities of the nitroamine in water and in 25 per cent. alcohol were determined at the laboratory temperature. The measurements were made either by treating known weights with a given quantity of solvent and weighing the undissolved material, or, with a somewhat less degree of accuracy, by titrating the saturated solutions with baryta in the presence of phenolphthalein:

100 grams of water dissolved 0·0715 gram at 11·5°.
100 ,, 25 per cent. alcohol dissolved 0·165 gram at 10°.
100 ,, ,, ,, ,, 0·167 ,,

The last number was obtained by titrating the saturated solution.

Barium 2 : 6-*Dibromonitroaminobenzene*, $(C_6H_3Br_2\cdot N\colon NO\cdot O)_2Ba,2\frac{1}{2}H_2O$.

This salt was prepared from the sodium salt and barium chloride; it crystallises in lustrous, nacreous plates, and is exceptionally soluble in water:

0·2060 at 105° lost 0·0125 H_2O. $H_2O = 6·06$.
0·2060 gave 0·0618 $BaSO_4$. $Ba = 17·6$.
$C_{12}H_6O_4N_4Br_4Ba,2\frac{1}{2}H_2O$ requires $H_2O = 5·9$; $Ba = 17·79$ per cent.

The molecular rearrangement of the nitroamine was studied under a variety of conditions. As solvents were used water, acetic acid (glacial, 80 per cent. and 20 per cent.), and aqueous alcohol (50 per cent. and 25 per cent.), and as acids hydrochloric and sulphuric acids. These varying conditions seemed not to cause any marked difference in the course of the transformation. The low solubility of the nitroamine in water renders this solvent unsuitable. Fifty per cent. aqueous alcohol dissolves the nitroamine freely, and at the same time is particularly adapted to effect an initial separation of the two anilines when a certain concentration of the nitroamine is used.

In the case of water and 25 per cent. alcohol, saturated solutions of the nitroamine were employed, but with the other solvents the solution contained 1·5 grams per 100 c.c. (v = 19·7). In the case of 50 per cent. alcohol, this concentration gave an initial separation consisting mainly of 2 : 6-dibromo-4-nitroaniline.

The strength of the acid has a marked effect on the speed of the change. Of the two acids mentioned above, sulphuric acid is therefore the least effective.

At low concentrations, the speed of the reaction is inconsiderable, but it is completed in twenty-four hours when the concentration of the acid is more than 8*N*.

Using 2*N*-hydrochloric acid (and 50 per cent. alcohol), a very pale yellow colour only appeared after seventy-two hours; with 4*N*-hydrochloric acid, the solution had assumed a yellow colour in twenty-four hours, but a separation of crystals of aniline only began after eight days; with 6*N*-hydrochloric acid, a faint colour developed in a few minutes, and a separation of crystals had begun in twenty hours; with 7*N*-hydrochloric acid, the separation after twenty-four hours was greater than with 6*N*.

The crystalline separation consisted in all cases of yellow needles, representing about one-third of the nitroamine when a solution in 50 per cent. alcohol was used at the concentration mentioned above, but only somewhat more than one-fifth if a saturated solution in 25 per cent. alcohol was employed.

The crystals from the latter solution softened at 118°, and were completely molten below 160°, whilst those from the former softened about 160°, and were completely molten at 185—190°. Repeated crystallisation of both materials from alcohol finally gave pure 2:6-dibromo-4-nitroaniline melting at 202—204°. The isomeric 2:4-dibromo-6-nitroaniline was isolated from the mother liquor as follows: the 50 per cent. aqueous alcohol was diluted with an equal volume of saturated sodium carbonate solution, whereupon yellow needles slowly separated, representing about one-third of the original nitroamine. Repeated crystallisation of the crystals (melting at 110—112°) slowly raised the melting point to 125—126°, the melting point of the dibromo-*o*-nitroaniline. Purification was, however, more satisfactorily effected by acetylating this material by boiling in acetic acid solution with acetyl chloride. The material, which separated on adding water, was recrystallised twice from benzene, from which solvent slender, colourless needles were obtained melting at 208—209°, the melting point of 2:4-dibromo-6-nitroacetanilide. They did not lower the melting point of the anilide prepared from 2:4-dibromoacetanilide.

The anilide dissolves readily in 10 per cent. aqueous potassium hydroxide, as do all such dihalogen-*o*- or -*p*-nitroacetanilides (Orton, Trans., 1902, **81**, 496). Hydrolysis was rapidly effected by boiling this solution, and as the hydrolysis proceeded the aniline separated in deep yellow or orange needles, which melted at 126—127° and did not affect the melting point of a specimen of the aniline prepared directly:

0·2104 gave 0·2356 AgBr. Br = 47·66.

$C_8H_6O_3N_2Br_2$ requires Br = 47·32 per cent.

Transformation of s-*Tribromo*-1-*nitroaminobenzene.*

The behaviour of solutions of this nitroamine in aqueous, aqueous alcohol, or aqueous acetic acid media, which are acidified with hydrochloric or sulphuric acid, resembles that of 2 : 6-dibromonitroaminobenzene in a remarkable manner. Similar strengths of acid determine approximately similar speeds of decomposition, and the proportion of *o*- and *p*-nitroaniline is approximately the same. The yellow crystals which first separate melt at 172—183°, whilst the material deposited after dilution with sodium carbonate melts below 110°. From the material of higher melting point, pure 2 : 6-dibromo-4-nitroaniline can be obtained, and from that of lower melting point the isomeric dibromo-*o*-nitroaniline, by the procedure which has been described above.

The great difference between the two nitroamines lies in the fact that bromine is set free during the conversion of the *s*-tribromoderivative into nitroanilines. Estimation of the bromine was not practicable in the complex mixtures dealt with.

Transformation of s-*Trichloronitroaminobenzene.*

With the lower concentrations of acid, decomposition of this nitroamine is far slower; with higher concentrations, large crystals of tetrachlorobenzoquinone are slowly deposited. The solution remains nearly colourless during the reaction, never acquiring the yellow colour indicative of the presence of the nitroanilines. *s*-Trichloroaniline was recognised in the mother liquor from the chloroanil by diluting largely, partly neutralising with sodium carbonate, and then extracting three times with chloroform. The residue remaining on evaporating the solvent was extracted with hot dilute alcohol, which left tetrachlorobenzoquinone undissolved. From this solution, *s*-trichloroaniline separated in colourless needles melting at 76°.

Reduction of Nitroamines in the Presence of Hydrobromic and Nitric Acids.

The presence of diazonium salts can always be recognised when the nitroamines have changed under the influence of hydrochloric or sulphuric acid, although the quantity is but small. In order to detect the diazo-compound, an aqueous solution of resorcinol is added to the liquid, the acidity of the solution being cautiously reduced by sodium carbonate; a slight precipitate of the azo-compound is formed, or, when the quantity is exceptionally minute, coloration alone results.

With hydrobromic and nitric acids, however, reduction to the diazo-compound becomes the chief reaction. The nitric acid is evidently reduced in the presence of alcohol, or even of acetic acid, to nitrous acid, which then reacts with the nitroamines in the usual way.

s-Trichloro- and *s*-tribromo-nitroaminobenzenes are rapidly and quantitatively reduced in 50 per cent. aqueous alcohol or acetic acid solution containing hydrobromic acid at concentrations of 5—6*N*, the solution assuming both the colour and odour of bromine. In the case of the *s*-trichloro-derivative, no precipitation occurs, and the diazo-compound can be isolated after removing bromine by coupling with β-naphthol or resorcinol. The trichlorobenzeneazonaphthol, after recrystallisation from acetic acid, melted at 144—145°, the pure compound melting at 145—146° (Orton and Smith, Trans., 1905, **87**, 395). Further, on adding alcohol to the mixture and warming, the diazo-compound can be converted into *s*-trichlorobenzene, a reaction which is quantitative under the conditions.

In the case of *s*-tribromonitroaminobenzene, the very low solubility of the diazonium perbromide, $C_6H_2Br_3{\cdot}N_2Br_3$, effected an approximately quantitative separation of the diazo-compound. The perbromide separated in long, orange needles, which decomposed at about 140°, and was recognised by its conversion into *s*-tribromobenzene by alcohol, by its coupling with β-naphthol in alcoholic solution with the formation of *s*-tribromobenzeneazonaphthol, and by giving a precipitate of silver bromide with alcoholic silver nitrate.

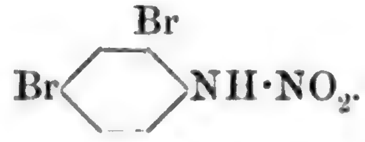
The 2:6-dibromonitroaminobenzene reacts in a more complicated way with hydrobromic acid, owing to the reduction to diazo-compound and the wandering of the nitro-group taking place simultaneously. Moreover, bromine, set free in the oxidation of the hydrobromic acid, converts some of the unchanged dibromonitroamine into *s*-tribromonitroamine, which is then in its turn reduced by hydrobromic acid. Using 50 per cent. alcohol and concentrations of hydrobromic acid 5—6*N*, the yellow, crystalline precipitate consists of a mixture of nitroanilines which have the usual properties, both the 2:6-dibromo-4-nitro- and the 2:4-dibromo-6-nitro-aniline being recognised and isolated. The mother liquor contained much diazo-compound, as indicated by the reaction with β-naphthol or resorcinol. *s*-Tribromodiazobenzene was detected by adding alcohol and distilling, when pure *s*-tribromobenzene (m. p. 119°) passed over. The detection of 2:6-dibromodiazobenzene, which should be present, would be a matter of considerable difficulty in the presence of a *s*-tribromo-derivative.

The use of nitric acid gives similar, but less distinct, results. *s*-Trichloronitroaminobenzene slowly decomposed in solution in 50 per cent. acetic acid containing nitric acid (which was freed from nitrous acid by carbamide nitrate) at a concentration of $9N$. The liquid developed very little colour, and, when all the nitroamine had disappeared, contained only the diazo-compound, which was isolated by coupling with β-naphthol.

With *s*-tribromonitroaminobenzene, a similar reaction takes place, but the evolution of bromine points to the replacement of bromine by the nitro-group. The small extent of this reaction, however, did not permit of the isolation of the dibromonitroanilines.

In the case of 2 : 6-dibromonitroamine, beyond the production of diazo-compound, no very decisive indications were obtained. If nitroaniline is formed by migration of the nitro-group (and such is not only probable, but is indicated by the colour which rapidly develops in the mixture), diazotisation would be expected to follow, owing to reduction of the nitric acid. The absence of separation of nitroaniline would be accounted for in this way.

2 : 4-*Dibromo*-1-*nitroaminobenzene*,



This nitroamine is prepared by a method which is a slight modification of that originally used by one of us (Orton, Trans., 1902, **81**, 806), in which a solution of the aniline in acetic acid was successively treated with nitric acid and acetic anhydride. The nitric acid, free from nitrous acid, was prepared from fuming nitric acid in the following way. The fuming acid was cooled by ice and treated with small quantities of powdered carbamide nitrate, whereupon it became colourless and at the same time diluted to 87 or 88 per cent. nitric acid.

Ten grams of the 2 : 4-dibromoaniline dissolved in 25 c.c. glacial acetic acid, cooled to the freezing point of the solution, are slowly added to a mixture of 5 c.c. of the nitric acid, prepared as above, 25 c.c. of acetic acid, and 25 c.c. of acetic anhydride, the temperature being maintained at the freezing point of the solution. The solution of nitric acid is prepared by adding the nitric acid slowly to the acetic acid and then introducing the acetic anhydride, the temperature being kept throughout as low as possible; with care, only traces of nitrous acid are formed. After admixture, the solution has a dull purple colour, and should contain no undissolved solid material. It is poured into 500 c.c. of ice-cold water, and the oil which separates extracted with chloroform, a small amount of diazonium salt alone remaining in the aqueous acid liquor. The chloroform solution is freed from acetic acid by shaking three times with small quantities of water, and then the nitroamine is extracted by means of aqueous sodium carbonate. The chloroform finally only contains a small quantity of 2 : 4-dibromo-6-nitroaniline. The solution of sodium carbonate is carefully titrated with 5 per cent. hydrochloric acid to remove excess of alkali, the mixture being left just alkaline. The liquid is then heated nearly to boiling point, and a warm solution of barium chloride is added in some excess of the quantity equivalent to a theoretical yield of nitroamine. The hot solution is filtered from any barium carbonate which may be precipitated, and on cooling deposits the *barium* salt of the nitroamine in large, colourless plates. The salt is very sparingly soluble in cold water, but can be readily recrystallised from boiling water:

0·5123 lost, over sulphuric acid, 0·0298 H_2O. $H_2O = 5·87$.

0·4343 anhydrous salt gave 0·1365 $BaSO_4$. $Ba = 18·56$.

$C_{12}H_6O_4N_4Br_4Ba,2\frac{1}{2}H_2O$ requires $H_2O = 5·83$ per cent.

$C_{12}H_6O_4N_4Br_4Ba$ requires $Ba = 18·84$ per cent.

The nitroamine is prepared from the barium salt as follows: 0·5 gram of the salt is dissolved in 100 c.c. of water at 30°, and a half per cent. solution of hydrochloric acid slowly added in some excess. The nitroamine begins immediately to crystallise out. When the mixture is cold, the nitroamine is collected, washed with water, and dried over sulphuric acid. It crystallises in lustrous, transparent plates, which are often greatly elongated; it melts at 65°:

0·1417 gave 0·1795 AgBr. $Br = 53·92$.

$C_6H_4O_2N_2Br_2$ requires $Br = 54·0$ per cent.

The nitroamine dissolves readily in all organic solvents with the exception of petroleum, from which solvent it crystallises in large, colourless plates. It dissolves very sparingly in cold water, yielding an acid solution, and can be recrystallised from water which has been saturated at 30°.

Transformation of the Nitroamine into 2 : 4-Dibromo-6-nitroaniline.—Solutions of the nitroamine appear to be permanent, remaining colourless for an indefinite period. Acidification with strong acids of the aqueous, aqueous acetic, or glacial acetic acid solutions brings about the migration of the nitro-group. For corresponding concentrations of acids, the speed of the change is greatest in the glacial acetic acid. The most suitable medium is a 1 to 5 per cent. solution of the nitroamine in glacial acetic acid to which has been added sufficient fuming hydrochloric acid to produce a 2*N*-solution. This mixture is kept at 25°, when the change is completed in a couple of hours. The only aniline produced is 2:4-dibromo-6-nitroaniline, but a small quantity of diazo-compound, arising from reduction of the nitroamine, can be detected in the usual way.

Preparation of 2 : 6-*Dibromoaniline.*

We have materially modified Heinichen's (*Annalen*, 1889, **253**, 275) method of preparing 2:6-dibromoaniline, and have thereby increased the yield. Following this author's procedure, sulphanilic acid in hydrochloric acid solution is brominated by means of sodium hypobromite, great care being taken to keep the temperature at 0°. No *s*-tribromoaniline should separate when the operation is correctly performed. To the resulting liquid, barium chloride is added, and then barium hydroxide until the mixture is neutral. The barium salt, $(NH_2 \cdot C_6H_2Br_2 \cdot SO_3)_2Ba,2H_2O$, separates immediately, 34·6 grams of sulphanilic acid yielding 85 grams of the salt. Concentration of the mother liquor gives a further small quantity.

In order to convert the dibromosulphanilic acid into 2:6-dibromoaniline, it is unnecessary to isolate the acid from the barium salt, which was the course followed by Heinichen. It is simpler to treat the hydrated salt, which has been dried in air, directly with sulphuric acid in the proportion: 20 grams of the salt, 72 grams of sulphuric acid, and 18 grams of water. Superheated steam is then passed through the mixture, which is maintained at a temperature of 160—180° in an oil-bath. 2:6-Dibromoaniline is formed by the hydrolysis of the sulphonic acid, and begins to distil over immediately. After two and a-half hours, when the hydrolysis is finished, the temperature is lowered to 120°, whereupon the sulphuric acid becomes more dilute, and the major part of the 2:6-dibromoaniline distils over. The yield of recrystallised material amounted to 84 per cent. of the theoretical.

UNIVERSITY COLLEGE OF NORTH WALES,
BANGOR.

LXVIII.—*The Action of Thionyl Chloride on the Methylene Ethers of Catechol Derivatives. Part II. Piperonyloin, Piperil, and Hydropiperoin.*

By GEORGE BARGER and ARTHUR JAMES EWINS.

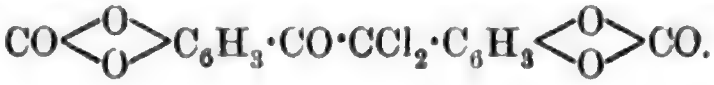
RECENTLY, one of us has shown (Trans., 1908, **93**, 563) that the methylene ethers of catechol derivatives are converted into the corresponding cyclic carbonates by heating with an excess of thionyl chloride to 180—200°. The same carbonates are formed by treatment of the chlorine derivatives, which result from the action of phosphorus pentachloride on the methylene ethers, with cold water, so that the effect of thionyl chloride is equivalent to that of phosphorus pentachloride and water.

In the previous paper, the action of thionyl chloride on piperonyl alcohol, piperonal, and piperonylic acid was described; in the present one, we deal with its action on compounds containing two catechol nuclei, namely, piperonyloin, piperil, and hydro- and *iso*hydro-piperoin. A large excess of thionyl chloride was found to be necessary, and serves as solvent from which the reaction product crystallises on cooling. With smaller quantities of thionyl chloride, whether in the presence or absence of an indifferent solvent, a great deal of decomposition always took place. Besides oxidising the methylene groups to carbonyl, thionyl chloride chlorinates the fatty chain linking the two benzene nuclei. The symmetrical grouping, $CH(OH)\cdot CH(OH)$, of hydropiperoin is thus converted into $CHCl\cdot CHCl$, but the asymmetrical grouping of piperonyloin, $CH(OH)\cdot CO$, is oxidised to $CCl_2\cdot CO$, so that the same substance is obtained as from the diketone piperil. Under the conditions employed in the production of cyclic carbonates, thionyl chloride was found to act in an analogous way on benzoin and benzil, oxidising the former, and converting both to dichlorobenzil, in the same way that phosphorus pentachloride acts on these substances.

Only in the case of the chloro-derivative from piperonyloin (and piperil) were we able to remove the chlorine from the fatty chain; we thus obtained a dicarbonate of tetrahydroxybenzil, and, from this, tetrahydroxybenzil itself; the constitution of the latter substance was proved by conversion into veratril, previously obtained from veratraldehyde.

EXPERIMENTAL.

3 : 4 : 3′ : 4′-*Dicarbonyldioxy-aa-dichlorodeoxybenzoin*,



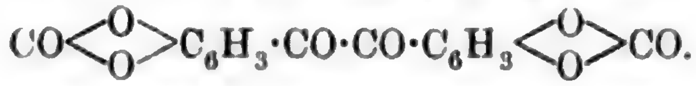
$$\mathrm{CO}{<}\substack{\mathrm{O}\\ \mathrm{O}}{>}\mathrm{C_6H_3\cdot CO\cdot CCl_2\cdot C_6H_3}{<}\substack{\mathrm{O}\\ \mathrm{O}}{>}\mathrm{CO}.$$

2·5 Grams of piperonyloin were heated with 10 c.c. of thionyl chloride in a sealed tube to 180° for seven hours. There was an unusually great pressure in the tube, and, on opening, sulphur dioxide and hydrogen chloride escaped. On cooling in a freezing mixture, the dark red solution deposited crystals, which were collected, washed with benzene, and recrystallised from xylene. Warty masses were obtained, which, after several crystallisations, separated in short, broad prisms melting at 191—192°. The yield was 60 per cent. of the theoretical:

0·1770 gave 0·3270 CO_2 and 0·0264 H_2O. C = 50·5 ; H = 1·7.
0·1421 „ (by fusion with potassium nitrate and sodium carbonate) 0·1094 AgCl. Cl = 19·0.
$C_{16}H_6O_7Cl_2$ requires C = 50·4 ; H = 1·6 ; Cl = 18·6 per cent.

The molecular weight was determined, by a microscopic method which we described some time ago (Trans., 1905, **87**, 1756), in glacial acetic acid at 85—90°, benzil being employed as standard. 0·157 Gram in 2·73 grams of acetic acid was intermediate between 0·16 mol. and 0·18 mol., whence M = 320—360, mean 340. $C_{16}H_6O_7Cl_2$ requires M = 381.

3 : 4 : 3′ : 4′-*Dicarbonyldioxybenzil*,



$$\mathrm{CO}<^{\mathrm{O}}_{\mathrm{O}}>\mathrm{C_6H_3{\cdot}CO{\cdot}CO{\cdot}C_6H_3}<^{\mathrm{O}}_{\mathrm{O}}>\mathrm{CO}.$$

0·5 Gram of the substance just described was boiled with 10 c.c. of anhydrous formic acid ; hydrogen chloride was evolved, and the substance gradually passed into solution. When no more hydrogen chloride was given off, the hot solution was filtered. On cooling, long, thin prisms separated, melting at 214—215° with effervescence, characteristic of catechol carbonates. After washing with cold water, until the washings were not coloured by ferric chloride, in order to remove a little of the corresponding free catechol derivative, the crystals were dried over sulphuric acid in a vacuum and analysed ; the melting point remained unchanged :

0·0828 gave 0·1776 CO_2 and 0·0228 H_2O. C = 58·5 ; H = 2·9.
$C_{16}H_6O_8$ requires C = 58·9 ; H = 1·8 per cent.

3 : 4 : 3′ : 4′-*Dicarbonyldioxybenzil* is readily hydrolysed by boiling with water, or by the addition of alkali, to tetrahydroxybenzil.

3 : 4 : 3′ : 4′-*Tetrahydroxybenzil*, $(HO)_2C_6H_3{\cdot}CO{\cdot}CO{\cdot}C_6H_3(OH)_2$.

The removal of the two chlorine atoms from the product of the reaction between thionyl chloride and piperonyloin, without hydrolysing the carbonate, was accomplished by formic acid, as stated above, but the other reagents employed for a similar purpose by Pauly (*Ber.*, 1907, **40**, 3096), namely, oxalic acid, succinic acid, and sulphuric acid, were found to be unsuitable for this purpose, no pure carbonate being obtainable. The crude reaction product, however, readily yielded tetrahydroxybenzil on boiling with water. One gram of 3 : 4 : 3′ : 4′-dicarbonyldioxy-*αα*-dichlorodeoxybenzoin was intimately mixed with 0·3 gram of anhydrous oxalic acid, and the mixture was carefully heated until there was no longer any evolution of gas. It was then boiled with water for several hours, a little animal charcoal being added towards the end. On concentrating the filtered solution, the substance crystallised; it was recrystallised from water and dried at 110°:

0·1588 gave 0·3573 CO_2 and 0·0510 H_2O. C = 61·4; H = 3·6.

$C_{14}H_{10}O_6$ requires C = 61·3; H = 3·6 per cent.

Tetrahydroxybenzil forms yellow prisms melting at 236°. It is readily soluble in hot water, from which it separates with two molecules of water of crystallisation:

0·4020, dried in desiccator until of constant weight, lost 0·0459 at 110°. H_2O = 11·4.

$C_{14}H_{10}O_6,2H_2O$ requires H_2O = 11·6 per cent.

Tetrahydroxybenzil is slightly soluble in cold water, readily so in alcohol, and dissolves in alkalis with an orange-red colour.

Tetrabenzoxybenzil, $C_{14}H_6O_6(CO\cdot C_6H_5)_4$.

0·5 Gram of tetrahydroxybenzil was dissolved in 5 grams of pyridine, and 2 grams (eight molecular proportions) of benzoyl chloride were added. After standing for eighteen hours, the solution was poured into dilute sulphuric acid. The amorphous solid which separated was crystallised from benzene and afterwards from ethyl acetate, and then formed long, thin needles melting at 202°:

0·1573 gave 0·4182 CO_2 and 0·0501 H_2O. C = 72·5; H = 3·5.

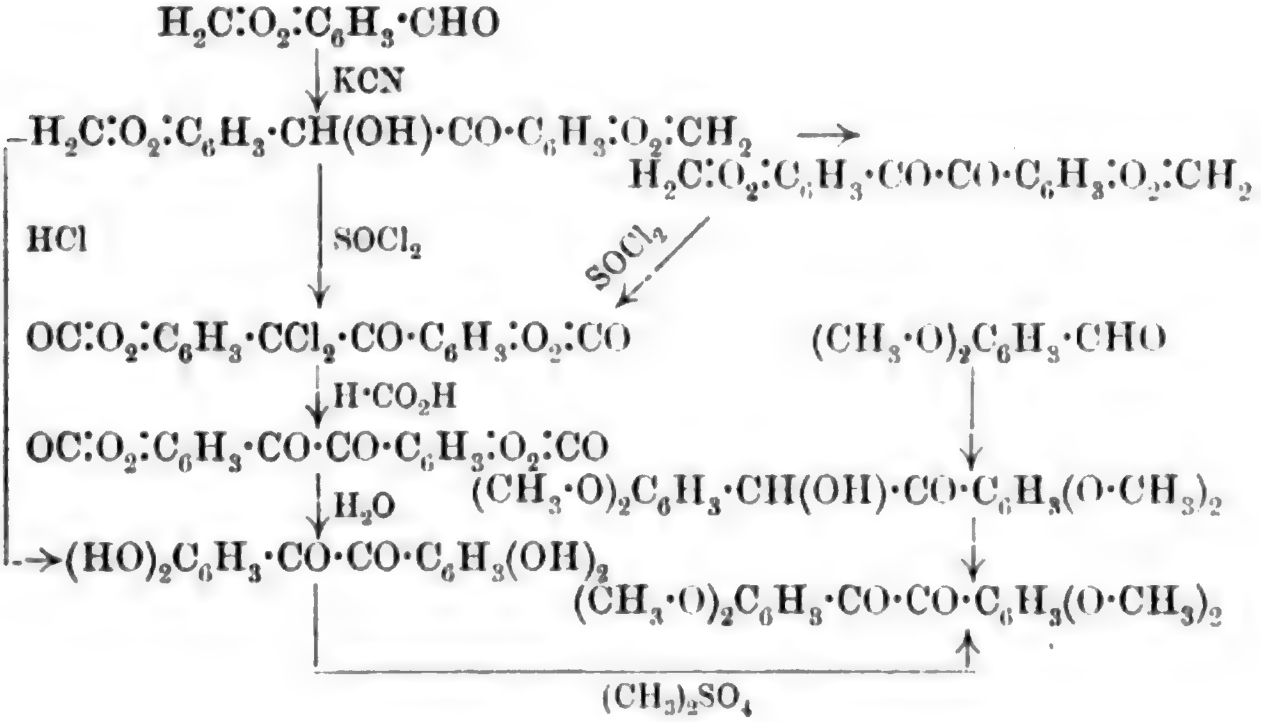
$C_{42}H_{26}O_{10}$ requires C = 73·0; H = 3·7 per cent.

Constitution of Tetrahydroxybenzil.

The constitution assigned above to this substance follows, firstly, from its method of preparation; secondly, from its direct production from piperonyloin, and thirdly, from its conversion into tetramethoxybenzil or veratril. The substance is produced directly from piperonyloin by heating with 1—2 per cent. hydrochloric acid to 180° for several hours, but the yield is extremely small (less than 10 per cent.); its identity with the substance obtained by thionyl chloride resulted from the melting point of the mixture.

The conversion of tetrahydroxybenzil into its tetramethyl ether (veratril) was carried out by dissolving 0·5 gram in the minimum quantity of methyl alcohol, and adding 0·7 c.c. (four molecular proportions) of dimethyl sulphate and then four molecular proportions of an aqueous 40 per cent. potassium hydroxide solution. The same amounts of dimethyl sulphate and potassium hydroxide were added a second time. On dilution with water, a bright yellow solid separated, which was crystallised from a mixture of 3 parts of alcohol and 1 part of benzene, and formed yellow prisms melting at 220°. This substance was identical with that obtained by oxidation of veratroin by ammoniacal cupric oxide, already described by Fritsch (*Annalen*, 1903, **329**, 37).

The transformation of the substances referred to above may be represented as follows:



$H_2C{:}O_2{:}C_6H_3{\cdot}CHO$
KCN
$H_2C{:}O_2{:}C_6H_3{\cdot}CH(OH){\cdot}CO{\cdot}C_6H_3{:}O_2{:}CH_2$
$H_2C{:}O_2{:}C_6H_3{\cdot}CO{\cdot}CO{\cdot}C_6H_3{:}O_2{:}CH_2$
HCl
$SOCl_2$
$SOCl_2$
$OC{:}O_2{:}C_6H_3{\cdot}CCl_2{\cdot}CO{\cdot}C_6H_3{:}O_2{:}CO$
$(CH_3{\cdot}O)_2C_6H_3{\cdot}CHO$
$H{\cdot}CO_2H$
$OC{:}O_2{:}C_6H_3{\cdot}CO{\cdot}CO{\cdot}C_6H_3{:}O_2{:}CO$
H_2O
$(CH_3{\cdot}O)_2C_6H_3{\cdot}CH(OH){\cdot}CO{\cdot}C_6H_3(O{\cdot}CH_3)_2$
$(HO)_2C_6H_3{\cdot}CO{\cdot}CO{\cdot}C_6H_3(OH)_2$
$(CH_3{\cdot}O)_2C_6H_3{\cdot}CO{\cdot}CO{\cdot}C_6H_3(O{\cdot}CH_3)_2$
$(CH_3)_2SO_4$

Action of Thionyl Chloride on Piperil.

As might be expected, the same chloro-derivative is formed by thionyl chloride from piperil as from piperonyloin; 0·47 gram piperil, heated to 180° with 2 c.c. of thionyl chloride for six hours, gave 0·3 gram of a substance melting at 190°, and identical with 3 : 4 : 3′ : 4′-dicarbonyldioxy-*aa*-dichlorodeoxybenzoin obtained from piperonyloin. The mixture of both specimens melted at 191°.

Action of Thionyl Chloride on Hydropiperoin and iso*Hydropiperoin.*

By heating either of the above substances with thionyl chloride on the water-bath, the same substance is produced, namely, 3 : 4 : 3′ : 4′-dimethylenedioxy-*aβ*-dichloro-*s*-diphenylethane,

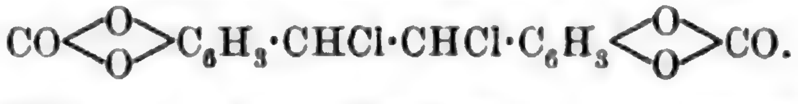
$$CH_2{:}O_2{:}C_6H_3{\cdot}CHCl{\cdot}CHCl{\cdot}C_6H_3{:}O_2{:}CH_2,$$

already obtained by Fittig and Remsen (*Annalen*, 1871, **159**, 144) by the action of acetyl chloride. At a much higher temperature, the methylene groups are also attacked.

Five grams of a crude mixture of hydropiperoin nd its isomeride were heated with 20 c.c. of thionyl chloride to 180° for five hours. The contents of the tube were cooled in a freezing mixture, and deposited crystals, which were recrystallised from benzene. The yield was only 0·51 gram:

0·1591 gave 0·2070 CO_2 and 0·0209 H_2O. C = 52·6; H = 2·2.
0·1506 ,, 0·1195 AgCl. Cl = 19·6.
$C_{18}H_8O_6Cl_2$ requires C = 52·3; H = 2·2; Cl = 19·3 per cent.

There can scarcely be any doubt that this substance is 3 : 4 : 3′: 4′-*dicarbonyldioxy-αβ-dichloro-s-diphenylethane*,



$$CO{<}\substack{O\\O}{>}C_6H_3\cdot CHCl\cdot CHCl\cdot C_6H_3{<}\substack{O\\O}{>}CO.$$

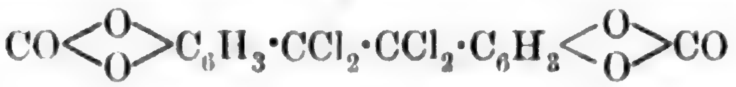
It melts at 260°, and is insoluble in water and sparingly soluble in most organic solvents; it dissolves in sodium carbonate or sodium hydroxide with an intense green colour. When the substance is boiled with water for some time, it yields a catechol derivative, as the solution gives a green coloration with ferric chloride. The catechol derivative is also formed by pyridine, and by benzoylation of the crude product by Einhorn's method a crystalline substance, melting at 123—124°, was obtained, free from chlorine and from nitrogen, which probably represented a benzoyl derivative of the catechol substance. The yield was too small for analysis, and, as the original chlorocarbonate could only be isolated in small quantity and in some experiments not at all, further work had to be abandoned.

The action of thionyl chloride on hydropiperoin is somewhat complex; only in one experiment was the above chloro-compound (m. p. 260°) obtained at once in an approximately pure condition. Generally, at temperatures from 160° upwards, a mixture of two kinds of crystals was obtained. 2·5 Grams of hydropiperoin gave, for instance, 0·52 gram of small, grey needles melting at 230—235°, and 0·45 gram of larger, glassy crystals of a much higher melting point.

The former of these two substances could not be obtained pure, but the latter, which preponderated when hydropiperoin was heated with thionyl chloride to 220°, was obtained sufficiently pure to leave no doubt as to its composition. It was almost insoluble in most organic solvents, dissolved sparingly in boiling xylene, and was moderately soluble in boiling nitrobenzene, from which it was recrystallised several times. It formed stout prisms melting at 310—311° (silver nitrate bath):

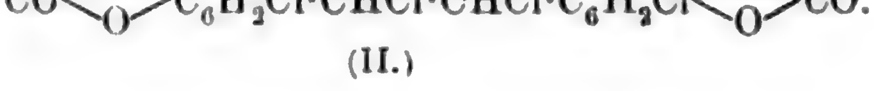
0·1473 gave 0·2411 CO_2 and 0·0208 H_2O. C = 44·6; H = 1·6.
0·1018 „ 0·1326 AgCl. Cl = 32·3.
$C_{16}H_6O_6Cl_4$ requires Cl = 44·0; H = 1·4; Cl = 32·5 per cent.

The substance is derived from the chloro-compound melting at 260°, by the introduction of two more chlorine atoms, and is therefore 3 : 4 : 3′ : 4′-*dicarbonyldioxytetrachloro-s-diphenylethane*; it is probably constituted according to one of the following formulæ:



$$CO{<}\substack{O\\O}{>}C_6H_3\cdot CCl_2\cdot CCl_2\cdot C_6H_3{<}\substack{O\\O}{>}CO$$

(I.)



$$CO{<}\substack{O\\O}{>}C_6H_2Cl\cdot CHCl\cdot CHCl\cdot C_6H_2Cl{<}\substack{O\\O}{>}CO.$$

(II.)

The substance is extremely stable (except towards alkalis, which attack the carbonyl groups). Boiling for several hours with formic acid scarcely alters it; in this respect, it differs markedly from the similar dichloro-derivative obtained from piperonyloin. According to formula I, the substance would be a derivative of *ααββ*-tetrachloro-*s*-diphenylethane, which is only attacked by glacial acetic acid at 200°; this suggested the following experiment.

One gram of the substance, $C_{16}H_6O_6Cl_4$, was suspended in 10 c.c. of glacial acetic acid and heated to 200° for two hours. On cooling, 0·37 gram of the unchanged material was collected. The almost black filtrate gave an intense catechol reaction with ferric chloride; the acetic acid was therefore distilled off under diminished pressure, and the residue was boiled with water and animal charcoal. The almost colourless filtrate deposited in a vacuum over sulphuric acid a minute quantity of long needles, which decomposed at 290—300° without melting. They were insoluble in cold water, but dissolved readily in alcohol; the alcoholic solution gave a green coloration with ferric chloride, changing to reddish-brown by a trace of alkali.

The fact that the whole of the chlorine was not removed, and that no tetrahydroxybenzil was obtainable, would indicate that some of the chlorine was in the benzene nuclei, and would therefore support formula II. The amount of substance available did not, however, allow us to investigate this point further.

THE WELLCOME PHYSIOLOGICAL RESEARCH LABORATORIES,
HERNE HILL, LONDON, S.E.

LXIX.—*The Solubility of Iodine in Water.*

By HAROLD HARTLEY and NORMAN PHILLIPS CAMPBELL.

THE solubility of iodine in water has been determined by a number of observers, and their results lead to very different values. For instance, at 25·5°, Meyerhoffer (*Zeitsch. physikal. Chem.*, 1888, **2**, 594) found 0·426 gram per litre, Noyes and Seidensticker (*Zeitsch. physikal. Chem.*, 1898, **27**, 388) at 25° found 0·3404 gram per litre, and McLauchlan (*Zeitsch. physikal. Chem.*, 1903, **44**, 687) at 25° found 0·279 gram per litre. Determinations at other temperatures have been made by Dossios and Weith (*Jahresber.*, 1869, 52, and 220), Wittstein (*Jahresber.*, 1857, i, 123), and Dietze (*Chem. Centr.*, 1898, i, 1094), and they do not show much better agreement.

Some of these discrepancies in the older values are probably due to the presence of impurities in the water or in the iodine, or to the use of soft glass vessels from which the water dissolved alkalis, as the solubility is greatly increased by any substance which gives rise to the formation of polyiodide in the solution.

In the experiments now described, care was taken to purify both iodine and water as far as possible, and the determinations were carried out in borosilicate glass apparatus, in which the conductivity of the water showed practically no change even after long standing.

Our result at 25° is in excellent agreement with Noyes and Seidensticker's experimental value, and we agree with the same authors in finding that the solubility of iodine in water does not increase progressively with time, as found by Dossios and Weith.

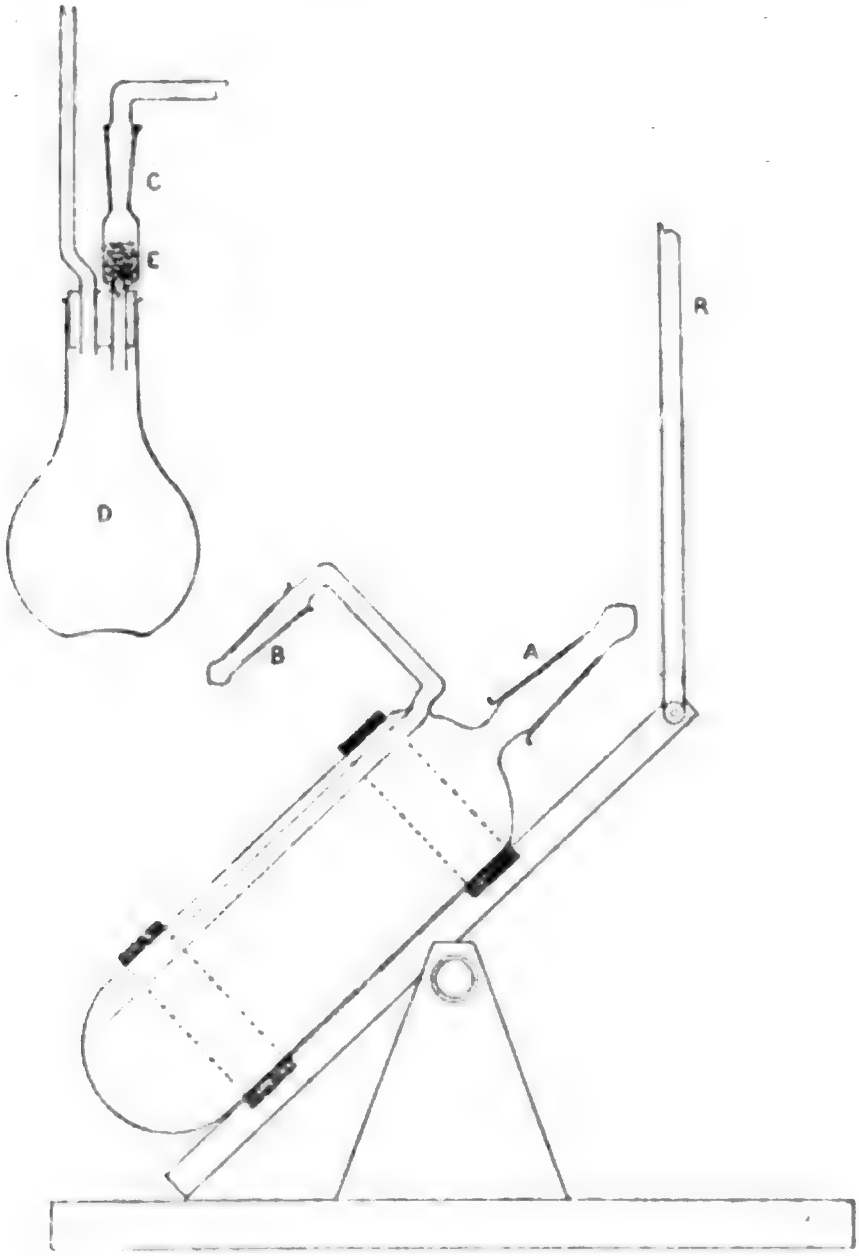
Materials.—The iodine was purified by Ladenburg's method (*Ber.*, 1902, **35**, 1256). Silver iodide was shaken with concentrated ammonia for twenty-four hours to dissolve any traces of silver chloride or bromide, then filtered and washed, and reduced with zinc and dilute sulphuric acid. The solution was treated with a mixture of oxides of nitrogen from nitric acid and starch, the precipitated iodide filtered, twice distilled in steam, then mixed with barium oxide and sublimed, and kept in a desiccator over calcium iodide. All the materials used were carefully tested to see that they were free from chlorine and bromine.

The water was distilled from alkaline and acid permanganate, and its specific conductivity varied from 1 to 1·5 gemmhos at the room temperature.

EXPERIMENTAL.

For the first series of experiments, iodine and water were stirred rapidly in a Jena glass flask, placed in a thermostat, but it was found that true saturation was never attained in an open flask, owing to the rapidity with which the iodine volatilised from the surface layer, so a closed apparatus was used of the form shown in the figure. It held about a litre of water, and to this was added excess of iodine, the glass caps, *A* and *B*, were then fixed firmly on with rubber tube and wire, and the vessel was rocked in a thermostat in the way shown in the figure, the connecting rod, *R*, having an eccentric attachment to a small flywheel driven by a motor. In order to withdraw a sample of solution for analysis, the vessel was detached from the rocker, both caps were removed, and the flask, *D*, was attached to *B* by means of the ground-joint, *C*, and immersed in the thermostat. The solution was then sucked over into *D*, any solid iodine being stopped by the glass-wool in *E*.

The flask, *D*, which had a ground-stopper, was weighed before and after the solution was drawn over, some solid potassium iodide being placed in it to diminish the volatility of the iodine and thus prevent loss. Excess of *N*/100 sodium arsenite solution was then added to the iodine solution, the amount being determined by weighing, and the small excess was titrated back with *N*/100-iodine solution, using starch as indicator. In working with *N*/100-sodium arsenite, it was found necessary to add about 12 grams of sodium bicarbonate per litre in order to secure a quick indication of the end point. The starch solution was sterilised in the way described by Treadwell. For each determination, a quantity of iodine solution, varying from 90 to 160 grams, was withdrawn in this manner.



In the following table, column I gives the time in hours, and column II gives the weight of iodine in grams per 1000 grams of solution :

Temp. 18°.		Temp. 25°.		Temp. 35°.		Temp. 45°.		Temp. 55°.	
I.	II.	I.	II.	I.	II.	I.	II.	I.	II.
32½	0·2782*	42	0·3318	46½	0·4631†	35	0·6452	42	0·9259*
57	0·2341	66¾	0·3393*	70½	0·4659*	47¼	0·6473*	53	0·9157*
97	0·2915	26	0·3371	94¼	0·4659*	60	0·6435‡	107	0·9233*
66	0·2998	47¼	0·3393*	—	—	71	0·6467*	147½	0·9163§
90	0·3006	71¾	0·3395*	—	—	—	—	—	—
98½	0·3130	—	—	—	—	—	—	—	—
39	0·2743*	—	—	—	—	—	—	—	—
69	0·2785*	—	—	—	—	—	—	—	—
113	0·2746*	—	—	—	—	—	—	—	—

* Value used in calculating mean.
‡ Slight uncertainty in titration.
† Stirring stopped during night.
§ Temperature not constant.

The mean values for the five temperatures are :

18°	0·2765	gram of iodine	per 1000	grams of	water
25	0·3395	,,	,,	,,	,,
35	0·4661	,,	,,	,,	,,
45	0·6474	,,	,,	,,	,,
55	0·9222	,,	,,	,,	,,

It will be seen that the solutions took from one to two days to reach the point of saturation even in a closed vessel. The results show fair agreement considering the possible experimental errors and the large temperature-coefficient of the solubility. The deviations at 18° must have been due to some impurity introduced during the first withdrawal of solution, as in the third series, when fresh material was introduced, the solubility fell to its original value.

The molecular heat of solution of iodine in water has been calculated by means of the formula

$$\log_e \frac{C_1}{C_2} = \frac{Q}{2}\left(\frac{1}{T_2} - \frac{1}{T_1}\right),$$

where C_1 and C_2 are the concentrations at temperatures T_1 and T_2, and Q is the molecular heat of solution, which is assumed to be constant between T_1 and T_2, a condition which is not strictly fulfilled.

Baxter, Hickey, and Holmes (*J. Amer. Chem. Soc.*, 1907, **29**, 127), from their determination of the vapour pressures of iodine between 0° and 55°, calculated its molecular heat of vaporisation to be approximately constant and equal to 15·1 Cals. ; the molecular heat of vaporisation from solution must be equal to the difference between heats of vaporisation and of solution.

The values are given in the following table :

Temp.	Mol. heat of solution in Cals.	Mol. heat of vaporisation from solution in Cals.
21·5°	5·09	10·01
30·0	5·82	9·28
40·0	6·44	8·66
50·0	7·38	7·72

Physical Chemistry Laboratory,
Balliol College and Trinity College,
Oxford.

LXX.—*The Sulphination of Phenolic Ethers and the Influence of Substituents.*

By Samuel Smiles and Robert Le Rossignol.

In a previous paper (Trans., 1906, **89**, 696), the authors showed that the interaction of thionyl chloride and phenetole takes place in three successive stages, which are marked by the formation of the sulphinic acid, sulphoxide, and sulphonium salt. The whole reaction may be formulated thus:

$$EtO{\cdot}C_6H_5 \longrightarrow EtO{\cdot}C_6H_4{\cdot}SO{\cdot}OH \longrightarrow (EtO{\cdot}C_6H_4)_2SO \longrightarrow (EtO{\cdot}C_6H_4)_3S{\cdot}OH.$$

To this process, where quadrivalent sulphur is introduced, we propose to apply the term sulphination in distinction to the name sulphonation which is given to the substitution of that element in the sexavalent condition.

In the communication above referred to, we were unable to isolate the phenetolesulphinic acid which should form the primary product of the reaction. We were limited to showing that this acid could be transformed by condensation with phenetole to a sulphoxide and sulphonium base, which were identical with the products obtained by the interaction of phenetole and thionyl chloride. It seemed desirable therefore to obtain a more direct proof that the sulphinic acid is the initial stage of sulphination. The object with which these experiments were undertaken was twofold, namely, (1) to show that a sulphinic acid is formed during the sulphination of an aromatic compound, and (2), since this result was achieved by employing a substituted phenolic ether, to study the effect of substitution on the course of this reaction. These may be considered separately.

Owing to the somewhat violent action of thionyl chloride and aluminium chloride on the phenolic ethers, we found it necessary to devise a milder sulphinating reagent which could be more easily controlled. We found gaseous sulphur dioxide and aluminium chloride to be the most suitable reagent. Whilst our experiments with this reagent were nearing completion, we communicated in June, 1906 (Proc., 1906, **22**, 158), an outline of the results to the Society. A few weeks later, we heard from Prof. Knoevenagel that he also was engaged on similar work, and he directed our attention to the fact that at his instance a patent had already been taken out (Knoll & Co. D.R.-P. 171789 Sept. 16, 1905) for the preparation of sulphinic acid by this method; but here no mention was made of the formation of sulphoxides or sulphonium bases. Since our experiments had for the greater part not dealt with the substances examined by Prof. Knoevenagel, we agreed with him roughly to divide the field of investigation.

The action of this reagent on benzene has been previously noticed by Friedel and Crafts (*Ann. Chim. Phys.*, 1888, [vi], **14**, 443), by Adrianowsky (*J. Russ. Phys. Chem. Soc.*, 1879, **11**, 119), and by Colby and Loughlin (*Ber.*, 1887, **20**, 195). The first-named investigators merely state that they obtained benzenesulphinic acid by passing gaseous sulphur dioxide into a warm mixture of benzene and aluminium chloride; they do not give the quantities of the reagents or the yield of acid. Adrianowsky led sulphur dioxide over hot aluminium chloride and thus obtained the compound $AlCl_3,SO_2$; this was found to react with warm benzene, giving benzenesulphinic acid. Colby and Loughlin, in describing their investigation of phenyl sulphoxide, mention that they obtained this substance by the action of sulphur dioxide on hot benzene and aluminium chloride. Finally, as above mentioned, Prof. Knoevenagel (*loc. cit.*) showed that sulphinic acids may be obtained in excellent yield by the action of gaseous sulphur dioxide on a mixture of an aromatic hydrocarbon and aluminium chloride; in the patent referred to, the example of benzenesulphinic acid is quoted. We have independently found (Proc., 1906, **22**, 158) that these reagents may be generally applied to the preparation of either aromatic sulphinic acids, sulphoxides, or sulphonium bases. It is shown in subsequent pages that the type and quantity of the products depend on the nature and position of the groups already attached to the aromatic nucleus. In some cases the reaction is confined to the preliminary stage, the sulphinic acid being then the sole product; in others the sulphination is more complete and the sulphonium base is formed, whilst with some substances the sulphination proceeds only as far as the intermediate stage, and with these the sulphoxide may preponderate.

The action of sulphur dioxide on a mixture of the aromatic substance and aluminium chloride takes place readily even at 0°. The mixture rapidly absorbs the gas, and in a short time becomes warm, evolving hydrogen chloride.

With regard to the mechanism of the reaction, it might be supposed that the gas on entering the solution is converted by the aluminium chloride into thionyl chloride, which would then act in the nascent state on the aromatic compound. This view, however, seems untenable. Baud (*Ann. Chim. Phys.*, 1904, [viii], **1**, 8) found that aluminium chloride and sulphur dioxide unite at the ordinary temperature, forming the compound $Al_2Cl_6,2SO_2$ (see also Adrianowsky, *loc. cit.*); he also showed that when this substance is heated to 80°, it decomposes into sulphur dioxide and the compound Al_2Cl_6,SO_2, and the latter on further heating to about 200° yields sulphur tetrachloride; but according to the above hypothesis the compound Al_2Cl_6,SO_2 when heated should yield thionyl chloride and an oxychloride of aluminium. Furthermore, the interaction of thionyl chloride, benzene, and aluminium chloride at the ordinary temperature gives (Colby and Loughlin, *loc. cit.*) phenyl sulphoxide, whilst sulphur dioxide under the same conditions furnishes benzenesulphinic acid alone.

The contrast between the action of this reagent and that of thionyl chloride can be seen in the cases of benzene and *m*-5-xylenol methyl ether. In both instances, thionyl chloride furnishes less sulphinic acid and more sulphoxide than is obtained with gaseous sulphur dioxide, and with the xylenol ether the yield of sulphonium salt is also greatly increased. In spite of the milder action of sulphur dioxide, we have not been successful in isolating phenetolesulphinic acid from the products of sulphination of phenetole; nevertheless we have been able to obtain the acid from more complex phenolic ethers. *p*-Cresol methyl ether yields the sulphinic acid and sulphoxide, whilst the methyl ether of *m*-5-xylenol gives the three types of product: sulphinic acid, sulphoxide, and sulphonium base. These facts, together with those already advanced (Trans., 1906, **89**, 696), furnish definite proof that the sulphinic acids are the primary products of sulphination.

The influence of substitution on the course of the reaction was followed by examining the behaviour of various phenolic ethers. The experiments were conducted in a roughly quantitative manner, and a summary of the results is appended in the following table. In the first column, the compounds submitted to sulphination are given, whilst in the second, third, and fourth the yields of sulphinic acid, sulphoxide, sulphonium chloride from 20 grams of material are shown:

Twenty grams of	Yield in grams of sulphonic acid.	Yield in grams of sulphoxide.	Yield in grams of sulphonium salt.
Benzene	10	none	none
Toluene	8	<1	<1
Anisole	none	7—8	15—16
Phenetole	,,	1—2	17—18
m-Cresol methyl ether	,,	3	16
Resorcinol dimethyl ether	,,	3*	12—16
Quinol dimethyl ether	,,	4*	none
,, ,, ,, ($SOCl_2$)	,,	15*	,,
p-Cresol methyl ether	3—4	12—14	,,
m-5-Xylenol methyl ether	7	1·5	trace
,, ,, ,, ($SOCl_2$)	1	12*	2

* Contain sulphide.

In each case the sulphination was carried out under as nearly as possible the same conditions; these together with the methods of isolating the products are described in the experimental part of this paper. The figures quoted for the yields are only approximate, but they are sufficient to show the relative amounts of each type of product formed during sulphination of each compound.

Constitution of the Products.

Before discussing the effect of substitution on the course of the reaction, it is necessary to consider the position taken up by the sulphinic group on combining with the aromatic nucleus in each of these substances.

Toluene.—The sulphinic acid obtained is identical with that prepared from *p*-toluidine; it is therefore the para-derivative.

Phenetole.—It has already been shown that with phenetole the sulphur group takes up the para-position with respect to the ethoxyl (Smiles and Le Rossignol, Trans., 1906, **89**, 698). This was demonstrated from the facts that the phenetyl sulphoxide obtained is also formed by condensation of phenetole-*p*-sulphinic acid with phenetole, and that it may be oxidised to phenetole-*p*-sulphone.

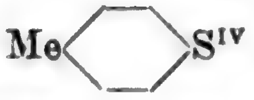
Anisole.—Similar facts have been collected to show that, also, with anisole, substitution takes place in the para-position. Anisylsulphoxide when oxidised yields the anisylsulphone which is obtained by methylation of phenol-*p*-sulphone. Further, Loth and Michaelis (*Ber.*, 1894, **27**, 2540), by the action of thionyl chloride and aluminium chloride in warm ethereal solution on anisole, obtained the anisyl sulphide which Mauthner (*Ber.*, 1906, **39**, 3593) has recently shown by synthesis from *p*-anisylmercaptan and *p*-iodoanisole to be the para-derivative.

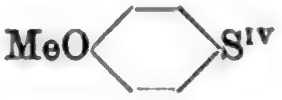
p-*Cresol Methyl Ether.*—Here the sulphinic group enters the ortho-position with respect to the methoxyl group. This is proved as follows. The methyl ether of *p*-cresolsulphinic acid may be oxidised in alkaline solution to a sulphonic acid, which is identical with that obtained by sulphonation of the ether. The same chloride and amide are furnished by the sulphonic acid from either source. Now Alleman (*Amer. Chem. J.*, 1904, **31**, 25; see also Metcalf, *ibid.*, 1893, **15**, 320) has shown that sulphonation of the ether takes place in the ortho-position with respect to the methoxyl group, yielding *p*-methoxytoluene-*m*-sulphonic acid. Hence the sulphinic acid formed from *p*-cresol methyl ether is *p*-methoxytoluene-*m*-sulphinic acid. Additional strength is given to this conclusion by the fact that Gattermann (*Ber.*, 1899, **32**, 1144), on treating the diazonium salt of *p*-methoxy-*m*-toluidine with copper powder and sulphurous acid, obtained a sulphinic acid of the same melting point as that furnished by direct sulphination. We have not, however, submitted these two products to a closer comparison.

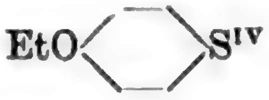
Quinol Dimethyl Ether.—Here the sulphinic group must occupy the ortho-position with respect to a methoxyl group.

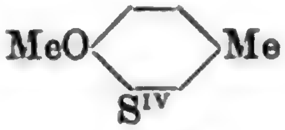
From these instances, it is clear that on sulphinating the phenolic ethers the quadrivalent sulphur group enters the same position as the sulphonic group during sulphonation, and, indeed, this is to be expected from the general rules of substitution. It is well known that sulphonation of phenetole yields either the ortho- or para-sulphonic acids or both, according to the conditions of the reaction, and it is worth remarking that we have already observed (Trans., 1906, **89**, 699) the formation of isomeric sulphonium salts during the interaction of thionyl chloride and phenetole.

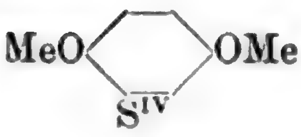
Although in the three remaining ethers, resorcinol dimethyl ether, *m*-cresol methyl ether, and *m*-5-xylenol methyl ether, we have not been able to obtain direct proof of the position of the entrant sulphur group, there is little doubt from the behaviour of the ethers previously described that this is introduced in the para-position with respect to the methoxyl group. In the case of *m*-cresol, the conclusion is confirmed by the results of sulphonation, which yield *m*-hydroxytoluene-*o*-sulphonic acid (Claus and Krauss, *Ber.*, 1887, **20**, 3089). Beyond the analogy with other ethers, furthur evidence is lacking to show the structure of the sulphinic derivatives of *m*-5-xylenol; it is probable that the sulphur group occupies the para-position with respect to the methoxyl, but for the present purpose it is immaterial whether it takes the para or ortho situation, in either case the quadrivalent sulphur has two adjacent groups in the ortho-position. The following formulæ represent the constitution of these substances:

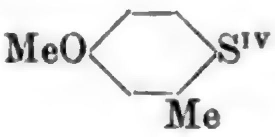


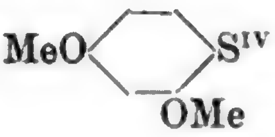


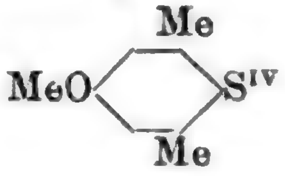












Discussion of Results.

The varying nature and amounts of the products obtained by sulphinating these ethers can be readily explained by considering the directing influence which the groups already attached to the benzene nucleus exert on the entrant quadrivalent sulphur group, and by the steric conditions under which the latter is placed. Although these influences are well known and often referred to by chemists, a few words on the sense in which we wish to apply them to the present question may not be out of place. By directing influence, we mean not only the guiding influence which a group exerts on another about to combine with the substance, but also the reactivity which it imparts to the benzene nucleus. On examining the parent substance, benzene, it seems that this is not very reactive, since only the sulphinic acid is formed; evidently, under the given conditions, benzene does not react with benzenesulphinic acid to give the sulphoxide. On the other hand, a derivative which contains a group of strong directing influence, such as methoxyl appears to be, will be inclined by virtue of its increased reactivity to yield the later stages of the reaction; at the same time, the sulphinic group is directed to a special position, which, in this case, is ortho or para to the methoxyl. Thus anisole, in contrast to benzene, furnishes a large amount of the sulphonium salt, a small quantity of *p*-anisyl sulphoxide, and no sulphinic acid.

With regard to the influence of steric* conditions, it is well known that often in aromatic compounds the reactivity of a group seems to be lessened if the ortho-position is occupied. In many reactions, notably the semidine change (Jacobson, *Annalen*, 1895, **287**, 97; 1898, **303**, 290), and the formation of rosanilines (Noelting, *Ber.*, 1889, **22**, 2573), these steric influences have been regarded from another standpoint: they are assumed to control the reaction in such a way as to avoid a product which contains accumulated ortho-substituents. It is this view which we adopt in the following discussion.

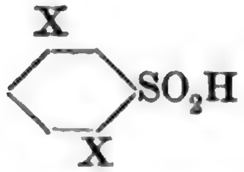
---

* We employ this term with some reserve, since Stewart and Baly (Trans., 1906, **89**, 489) have shown that the differences in reactivity of substituted quinones which have usually been ascribed to steric influences are due to quite different causes.

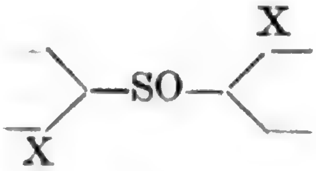
As already explained, it seems that in a substance which contains a group of strong directing influence the tendency will be to form the sulphonium base, but if the sulphur group enters the ortho-position with respect to a group already present, the reaction will be to a certain extent restrained, since ortho-substitution increases on passing through the successive stages. It is clear, then, that directing and steric influences will oppose one another, and, at any rate in the cases which we have examined, we think that by this conflict the varying products of sulphination can be satisfactorily explained.

With phenetole and anisole, substitution takes place in the para-position with respect to the methoxyl or ethoxyl group, and, there being no substituent in the ortho-position to the quadrivalent sulphur, the sulphination proceeds undisturbed by steric influences. The product is almost entirely sulphonium salt.

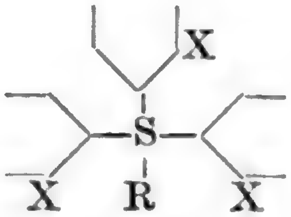
In the next pair of ethers, those of *p*-cresol and quinol, the sulphinic group takes up the ortho-position with respect to the methoxyl. The sulphinic acid (I), sulphoxide (II), and sulphonium base (III), which form the three successive stages of the reaction, would have the configurations:



(I.)



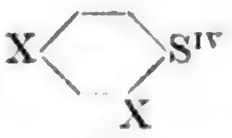
(II.)



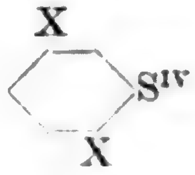
(III.)

and it is evident that, as the reaction proceeds, ortho-substituents are accumulated. With these ethers, the sulphonium salt is not formed during sulphination under the given conditions, the product consists chiefly of sulphoxide, and, in the case of *p*-cresol, an appreciable quantity of sulphinic acid. This suppression of the sulphonium salt is clearly due to the inhibiting action of the ortho-substitution, which attains the maximum at this stage.

Turning now to the ethers of resorcinol and *m*-cresol, we again find that the sulphinic group takes up an ortho-position with respect to methyl or methoxyl, and the configuration of the three products will be as before, the sulphoxide being doubly ortho-substituted, and the sulphonium salt trebly so. The steric relations in these substances are therefore similar to those in the above-mentioned ethers of *p*-cresol and quinol, but the products of sulphination are very different. In both cases, the chief product is the sulphonium salt, with a very small quantity of sulphoxide. Here it is evident that the steric inhibition is overcome by the directing influences of the methyl and methoxyl groups, and it will be seen in resorcinol and *m*-cresol methyl ether (I) that these reinforce one another at the point of substitution,



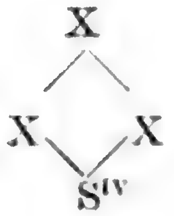
(I.)

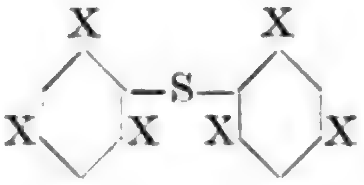


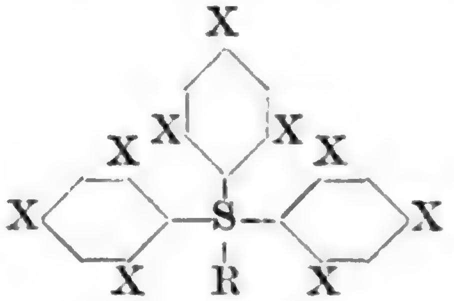
(II.)

whilst with quinol and *p*-cresol methyl ether (II) they do not. In the latter pair of ethers, the inhibiting effect of triple ortho-substitution is sufficient to overcome the comparatively weak directing influences but in the first-named ethers the directing influences are strengthened and the steric effect is in turn overcome.

The next ether, that of *m*-5-xylenol, shows yet a different behaviour. The three stages in the sulphination of this substance would have the configuration:







whence it is seen that the sulphinic acid would contain two ortho-substituents, the sulphoxide four, and the sulphonium base six. In comparison with *m*-cresol ether, the directing influences are strengthened, since the three substituents reinforce one another; but at the same time the steric inhibition is greatly augmented by the increased ortho-substitution, and its action is now sufficient to affect the course of the sulphination. Thus it is found that the sulphinic acid appears as the chief product, whilst the sulphonium base is almost completely suppressed, less than 1 gram of this being formed from 20 grams of the ether. From the same amount of *m*-cresol ether, 16 grams of sulphonium salt were obtained, and the sulphinic acid could not be detected.

The ethers of phenol, *m*-cresol, and *m*-5-xylenol thus form a series in which both directing and steric influences increase. In the first two substances, the directing influences are dominant, but with the third, as mentioned above, steric hindrance comes into play. The effect of steric hindrance may also be brought out by lessening the directing influences, as on passing from *m*-cresol to *p*-cresol. The latter substance yields no sulphonium salt.

It is of some interest to compare the behaviour of toluene and phenetole. With the former substance the second and third stages of the reaction are almost suppressed, whilst with the ether the sulphonium salt is formed in large quantity. Evidently this is due to the weaker directing influence of the methyl group, the steric relations in the two cases being similar.

Finally, we wish to remark that when it is stated that the sulphonium salt is not formed, we do not necessarily mean that this does not exist. Thus, in the case of *p*-cresol ether, it is shown that the use of a stronger condensing reagent than aluminium chloride readily furnishes the sulphonium base. It should be further noticed that a different sulphinating agent may lead to very different results, and this can be seen by comparing the action of sulphur dioxide with that of thionyl chloride in *m*-5-xylenol ether. The latter agent increases the yield of the sulphonium salt and lessens that of the sulphinic acid. In fact, what has been said of the sulphination of these phenolic ethers only refers to the reaction as carried out under the special conditions described in the experimental part of this paper.

EXPERIMENTAL.

In all the subsequent experiments, unless otherwise stated, the sulphination was carried out as follows. The liquid to be sulphinated was first gradually mixed with an equal weight of finely-powdered aluminium chloride. During the process, considerable heat was developed, hence the contents of the flask were thoroughly cooled in order to avoid hydrolysis of the phenolic ether. The vessel having been immersed in melting ice, gaseous sulphur dioxide was allowed to bubble through the liquid contents, the passage of the gas being regulated so as to confine the temperature of the solution below 15°. The process was continued until the mixture was saturated or had become solid. Finally, the product was set aside at the atmospheric temperature for two hours, and then decomposed with powdered ice or cold water. Usually the process of sulphination occupied from six to eight hours.

The method of isolating the products was varied according to the requirements of each case. Generally the acid liquid obtained by decomposing the product of sulphination was extracted with chloroform in which the three substances sulphinic acid, sulphoxide, and sulphonium chloride are soluble.

The presence of either of these products was established by the isolation and analysis of the substance in question. On the other hand, the conclusion that they were absent rests on a rather less firm basis. The absence of the sulphinic acid was inferred from the results of examining the alkaline extract from the chloroform solution. The sulphonium salts were tested for by adding aqueous chloroplatinic acid to the original acid liquid or to the aqueous extract from the chloroform solution; the platinichlorides of these bases are very sparingly soluble in water, and if no precipitate was obtained in applying this test it was inferred that the base in question was absent. Since these tests are by no means quantitative, any negative conclusion drawn from them is clearly somewhat insecure. Hence, when it is mentioned that neither sulphinic acid nor sulphonium base are present, the statement is made with some reserve; the substances may occur in very small quantity, but far too small to be isolated, and certainly not sufficient to affect the general conclusions drawn from these experiments.

Benzene.

Benzenesulphinic Acid.—Sulphination as above. On treatment with ice and hydrochloric acid, the mass furnished a pale yellow solid, which was collected and dissolved in dilute aqueous sodium hydroxide. Benzenesulphinic acid was precipitated from this alkaline solution by the addition of dilute mineral acid. Twenty grams of benzene yielded 10 grams of the acid. Neither sulphoxide nor sulphonium salt were observed in the product of sulphination under the above conditions. On account of its cheapness and the ease with which it is carried out, this method of preparing benzenesulphinic acid is superior to the reduction of the sulphonic chloride or to the decomposition of benzenediazonium salts with copper powder.

Toluene.

Toluene-p-*sulphinic Acid.*—Sulphination as above. By decomposing the product with water and hydrochloric acid, a yellow, solid mass was obtained; this was dissolved in chloroform, and the solution was extracted with aqueous sodium hydroxide. The alkaline liquid was mixed with excess of dilute sulphuric acid and cooled; the toluenesulphinic acid which separated (8 grams) was collected and recrystallised, and it finally melted at 84—85°. A mixture of this with toluene-*p*-sulphinic acid, prepared from *p*-toluidine, melted at the same temperature. Small quantities, less than one gram, of sulphoxide and sulphonium chloride were respectively obtained from the chloroform solution and from the original acid liquid. The presence of the sulphonium salt in the latter was recognised by precipitation with chloroplatinic acid. These substances were not closely examined.

Anisole.

Anisyl Sulphoxide, $(C_6H_4{\cdot}OMe)_2SO$, *and Trianisylsulphonium,* $(C_6H_4{\cdot}OMe)_3S{\cdot}$.

—Sulphination as usual. The product was slowly poured into cold water, and the resulting liquid, after the usual addition of acid, was repeatedly extracted with ether. The united ethereal extracts were shaken with dilute aqueous alkali hydroxide, and, on acidifying this, a small quantity of phenol was obtained, but no sulphinic acid was detected.

Anisyl Sulphoxide.—The ethereal solution was evaporated, and, after anisole had been removed by distillation in a current of steam, the residue was collected and dried. The product, anisyl sulphoxide, was almost pure; when recrystallised from hot ethyl acetate, it formed colourless prisms which melted at 93—94° (Loth and Michaelis, *Ber.*, 1894, **27**, 2540, give 96°). Analysis yielded the following data:

0·2390 gave 0·5599 CO_2 and 0·1251 H_2O. C = 63·89; H = 5·81.
0·2355 „ 0·1884 $BaSO_4$. S = 12·59.
$C_{14}H_{14}O_3S$ requires C = 64·12; H = 5·34; S = 12·21 per cent.

Trianisylsulphonium.—The aqueous layer from the original ethereal extract was evaporated on the water-bath until a considerable quantity of oil had separated. The liquid was cooled, and then extracted with chloroform. Finally, the chloroform solution was distilled, and the oily residue of sulphonium chloride was dried in the steam-oven. Trianisylsulphonium chloride, when set aside at the ordinary temperature, gradually solidifies to a mass of colourless needles, which are soluble in water, alcohol, or chloroform. For analysis, the salt was converted into the platinichloride.

Trianisylsulphonium platinichloride separates from a warm mixture of alcohol and epichlorohydrin in orange needles which melt at 221°:

0·2197 gave 0·3629 CO_2 and 0·0789 H_2O. C = 45·04; H = 3·99.
0·2513 „ 0·0438 Pt. Pt = 17·42.
$C_{42}H_{42}O_6Cl_6S_2Pt$ requires C = 45·24; H = 3·77; Pt = 17·5 per cent.

Twenty grams of anisole yielded 8 grams of anisyl sulphoxide and 15 grams of trianisylsulphonium chloride. In another experiment with the same quantity of anisole, 7 grams of sulphoxide and 16 grams of sulphonium chloride were obtained. In neither case was anisylsulphinic acid detected.

Anisylsulphone, $(C_6H_4{\cdot}OMe)_2SO_2$. (1) *Oxidation of Anisyl Sulphoxide.*—The sulphoxide was treated with potassium permanganate in glacial acetic acid solution (see Smiles and Le Rossignol, *loc. cit.*). The product, when recrystallised from alcohol, formed colourless prisms which melted at 129° (Loth and Michaelis, *loc. cit.*, give 120°, and Annaheim, *Annalen*, 1874, **172**, 36, gives 130°).

(2) *Methylation of* p-*Phenolsulphone.*—The methylation was effected with an alkaline solution of methyl iodide in methyl alcohol. The recrystallised product melted at 129°, and was identical with the above, since a mixture of the two melted at the same temperature:

0·2558 gave 0·2050 $BaSO_4$. S = 11·93

$C_{14}H_{14}O_4S$ requires S = 11·51 per cent.

Phenetole.

Phenetyl Sulphoxide, $(C_6H_4{\cdot}OEt)_2SO$, *and Triphenetylsulphonium*, $(C_6H_4{\cdot}OEt)_3S{\cdot}$.—Sulphination as above. The reaction product was worked up by a process similar to that described with anisole. The products, phenetyl sulphoxide and triphenetylsulphonium chloride, were found to be identical with those obtained by the action of thionyl and aluminium chlorides on phenetole (Smiles and Le Rossignol, *loc. cit.*). Two experiments, each with 20 grams of phenetole, furnished respectively 1 gram of sulphoxide with 17 grams of sulphonium chloride, and 2 grams of sulphoxide with 18 grams of sulphonium chloride.

m-*Cresol Methyl Ether.*

m-*Methoxytolyl Sulphoxide*, $(C_6H_3Me{\cdot}OMe)_2SO$, *and Tri*-m-*methoxytolylsulphonium*, $(C_6H_3Me{\cdot}OMe)_3S{\cdot}$.—The sulphination and method of treatment were the same as with anisole. The sulphoxide was isolated as a pale yellow oil; this was covered with dry ether, and set aside at the ordinary temperature. After the lapse of two weeks, the substance crystallised in colourless prisms, which were collected and purified from ethyl alcohol. m-*Methoxytolyl sulphoxide* melts at 83—84°, is soluble in hot ethyl acetate or alcohol, and gives a deep violet solution with concentrated sulphuric acid:

0·1589 gave 0·3840 CO_2 and 0·0844 H_2O. C = 65·90; H = 5·90.
0·2264 „ 0·1484 $BaSO_4$. S = 11·32.

$C_{16}H_{18}O_3S$ requires C = 66·20; H = 6·20; S = 11·03 per cent.

The crude sulphonium chloride formed a viscous liquid which did not show signs of crystallisation until it had remained four or five weeks under dry ether. It was converted into the platinichloride.

m-*Methoxytotylsulphonium platinichloride* forms orange-coloured plates which melt at 138—140°:

0·1990 gave 0·3501 CO_2 and 0·0829 H_2O. C = 47·9; H = 4·62.
0·1646 „ 0·0272 Pt. Pt = 16·52.

$C_{48}H_{54}O_6Cl_6S_2Pt$ requires C = 48·08; H = 4·58; Pt = 16·27 per cent.

Twenty grams of *m*-cresol methyl ether furnished 3 grams of sulphoxide and 16 grams of sulphonium base. No sulphinic acid was detected.

Resorcinol Dimethyl Ether.

tris-m-*Dimethoxyphenylsulphonium*, $(C_6H_3{\cdot}OMe)_3S{\cdot}$.—Sulphination as usual. The product was decomposed with ice-water, and then separated from unchanged phenolic ether by distillation in a current of steam. The residue was repeatedly extracted with hot water. The united extracts were filtered to remove small quantities of oily impurity, and were then set aside to cool.

The sulphonium chloride separated at first as an oil, but later in the crystalline form. When the liquid had cooled, the solid was collected.

tris-m-*Dimethoxyphenylsulphonium chloride* separates from warm moist acetone in flocculent aggregates of minute needles which melt at 129—130°. The substance is sparingly soluble in cold acetone or water, and extremely so in alcohol. It contains water of crystallisation; an air-dried sample was heated to constant weight at 110°, when it was found that:

0·1697 lost 0·0266 H_2O. $H_2O = 15{\cdot}67$.
0·1663 „ 0·0262 H_2O. $H_2O = 15{\cdot}75$.
$C_{24}H_{27}O_6ClS,5H_2O$ requires $H_2O = 15{\cdot}81$ per cent.

Determinations of halogen and of sulphur were made in the air-dried substance:

0·2481 gave 0·0652 AgCl. Cl = 6·49.
0·2419 „ 0·1076 $BaSO_4$. S = 6·10.
$C_{24}H_{27}O_6ClS,5H_2O$ requires Cl = 6·24; S = 5·63 per cent.

The anhydrous salt was also analysed:

0·1431 gave 0·3134 CO_2 and 0·0762 H_2O. C = 59·72; H = 5·91.
$C_{24}H_{27}O_6ClS$ requires C = 60·19; H = 5·64 per cent.

This sulphonium chloride gives an intensely reddish-violet solution with concentrated sulphuric acid.

The *platinichloride* was isolated as a flesh-coloured, crystalline powder, which was insoluble in water. It melts at 153—155°:

0·1852 gave 0·0273 Pt. Pt = 14·74.
$C_{48}H_{54}O_{12}Cl_6S_2Pt$ requires Pt = 15·06 per cent.

The residue from which the chloride had been extracted with water consisted of a pale brown, amorphous mass. This apparently contained at least two substances, one of which was soluble in hot alcohol, and the other quite insoluble; but, since attempts to purify them were not successful, it remains doubtful at present whether either was the required sulphoxide. Both substances imparted a reddish-violet colour to concentrated sulphuric acid.

In the above method of treatment, the product of sulphination is submitted to distillation with steam, and for this reason the process would not be suitable for isolating the sulphinic acid, should it be formed, since substances of this class are readily decomposed by hot aqueous mineral acids. Hence another experiment was performed in which the sulphinic acid was especially sought for, but none could be found.

Twenty grams of resorcinol dimethyl ether yielded in two different experiments 15—16 grams and 12 grams of sulphonium chloride. The formation of sulphoxide could not be proved, but it probably occurs in small amount.

Judging from analogy to quinol dimethyl ether (see later), the amorphous mass above referred to probably consists of a mixture of sulphide and sulphoxide.

p-*Cresol Methyl Ether.*

Sulphinic Acid, $MeO{\cdot}C_6H_3Me{\cdot}SO_2H$ ($Me : OMe : SO_2H = 1 : 4 : 3$), *and Sulphoxide*, $(MeO{\cdot}C_6H_3Me)_2SO$.—Sulphination as usual. The mixture of aluminium salts was decomposed in the usual manner with ice-water and hydrochloric acid. The sulphinic acid and sulphoxide now appeared as a crystalline suspension in the acid liquid; they were removed by extraction with chloroform. *p*-Methoxytoluene-*m*-sulphinic acid was isolated by first shaking the chloroform solution with aqueous sodium carbonate and then acidifying the latter with dilute mineral acid. After recrystallisation from hot water, it melted at 96—97° (Gattermann, *Ber.*, 1899, **32**, 1144, gives 97°):

0·2047 gave 0·3865 CO_2 and 0·0998 H_2O. $C = 51{\cdot}49$; $H = 5{\cdot}40$.
$C_8H_{10}O_3S$ requires $C = 51{\cdot}6$; $H = 5{\cdot}37$ per cent.

This acid gives a bright blue solution with concentrated sulphuric acid.

Oxidation of p-*Methoxytoluene*-m-*sulphinic Acid to the Sulphonic Acid*, $MeO{\cdot}C_6H_3Me{\cdot}SO_3H$.—A solution of the acid in excess of aqueous alkali hydroxide was warmed on the water-bath with the calculated amount of potassium permanganate. Towards the end of the reaction, alcohol was added to remove the green colour. The liquid was then successively filtered, neutralised with carbon dioxide, and evaporated to dryness. The sulphonyl chloride was prepared from the mixture of alkali salts; it separated from acetone in large, colourless plates which melted at 83—84°. When set aside with cold strong ammonia for forty-eight hours, the chloride furnished an amide melting at 182°.

Alleman (*loc. cit.*), by sulphonation of *p*-cresol methyl ether, obtained a sulphonic acid which he showed to be of the structure $MeO{\cdot}C_6H_3Me{\cdot}SO_3H$ ($Me : OMe : SO_3H = 1 : 4 : 3$). According to the same author, the chloride and amide of this acid melt respectively at 83·5—84° and 180—181°. We prepared these substances and were able to confirm the above temperatures of fusion. We also found that a mixture of the chloride or amide and the corresponding derivative prepared from the sulphinic acid melts at the same temperature as the pure substance from either source; hence oxidation of the sulphinic acid yields the sulphonic acid of the above constitution.

The chloroform solution from which the sulphinic acid had been extracted was dried and then distilled. The residue of almost pure sulphoxide was oily, but it immediately solidified on contact with dry ether. p-*Methoxytoluene sulphoxide*, $(MeO{\cdot}C_6H_3Me)_2SO$, forms shining prisms, which melt at 133—134° and are soluble in hot ethyl acetate or alcohol. With concentrated sulphuric acid, it gives a deep violet solution, which is decolorised by the addition of *p*-cresol methyl ether:

0·2938 gave 0·7089 CO_2 and 0·1654 H_2O. C = 65·81; H = 6·26.
0·2268 „ 0·1839 $BaSO_4$. S = 11·13.
$C_{16}H_{18}O_3S$ requires C = 66·20; H = 6·2; S = 11·03 per cent.

No sulphonium chloride could be detected in the product of sulphination.

From 20 grams of *p*-cresol methyl ether, 4 grams of sulphinic acid and 14 grams of sulphoxide were obtained. In another experiment, the yield of acid was about 3·5 grams and of sulphoxide 12 grams.

tris-p-*Methoxytolylsulphonium*, $(MeO{\cdot}C_6H_3Me)_3S{\cdot}$.—*p*-Cresol methyl ether was slowly mixed with a solution of the sulphoxide in concentrated sulphuric acid. When sufficient phenolic ether had been added to change the colour to pure red, the solution was poured into a large bulk of ice-cold water. The sulphonium sulphate then separated as a semi-solid precipitate, which was converted in aqueous solution into the chloride. The addition of chloroplatinic acid to the latter yielded tris-p-*methoxytolylsulphonium platinichloride* as a flesh-coloured precipitate which melted at 230—231°:

0·1511 gave 0·2653 CO_2 and 0·0590 H_2O. C = 47·88; H = 4·33.
0·1878 „ 0·0300 Pt. Pt = 15·97.
$C_{48}H_{54}O_6Cl_6S_2Pt$ requires C = 48·08; H = 4·5; Pt = 16·27 per cent.

The substance is insoluble in water or alcohol.

Quinol Dimethyl Ether

A mixture of equal weights of the phenolic ether and finely-powdered aluminium chloride was covered with carbon disulphide. Sulphination was then conducted as usual, fresh carbon disulphide being added from time to time to keep the mass sufficiently liquid to allow the passage of the gas. The product was a stiff brown mass; it was decomposed with ice. Since special tests did not reveal the presence of sulphinic acid, the contents of the flask were distilled in a current of steam until the quinol ether ceased to pass over. The remaining oil was separated from the acid mother liquor by shaking with chloroform, in which it dissolved readily. The chloroform solution was evaporated after repeated washing with water, and the residual oil was covered with ether and set aside in a desiccator. In about two weeks, it had solidified to a pale yellow, amorphous mass, which on further investigation proved to be a mixture.

The more soluble constituent was removed by extraction with hot alcohol, from which it was precipitated by addition of water. The amorphous solid was redissolved in acetone, and, after the pale green solution had been boiled with animal charcoal, it was filtered and again precipitated with water. The substance was evidently *p*-dimethoxyphenyl sulphide, since analysis yielded the following result:

0·1573 gave 0·3594 CO_2 and 0·0797 H_2O. C = 62·3; H = 5·62.

$C_{16}H_{18}O_4S$ requires C = 62·74; H = 5·88 per cent.

The colourless, amorphous substance thus obtained melts at 97—100°, and is soluble in acetone or hot alcohol. The insoluble constituent of the mixture was boiled with water to remove the aluminium salts, to which it clung tenaciously. Thus p-*dimethoxyphenyl sulphoxide* was obtained as a colourless, amorphous powder melting at about 200°. It dissolves in concentrated sulphuric acid with an intense emerald-green colour, which is removed by the addition of phenetole. It is insoluble in alcohol and sparingly so in hot acetone:

0·2048 gave 0·4470 CO_2 and 0·0980 H_2O. C = 59·52; H = 5·32:

$C_{16}H_{18}O_5S$ requires C = 59·62; H = 5·55 per cent.

The yield of these substances was comparatively small, the weight of the mixture obtained from 20 grams of phenolic ether being only 4 grams. No sulphonium salt could be detected.

The action of thionyl chloride and aluminium chloride on the quinol ether was also investigated. Thionyl chloride was gradually mixed with a solution of quinol dimethyl ether in carbon disulphide to which aluminium chloride had been added. The mixture of sulphide and sulphoxide furnished by 27 grams of the ether weighed 22 grams, and, from this, 8 grams of sulphide and 12 grams of sulphoxide were isolated. Again, neither sulphinic acid nor sulphonium salt could be detected in the products.

m-5-*Xylenol Methyl Ether.*

Sulphinic Acid, $MeO\cdot C_6H_2Me_2\cdot SO_2H$, *Sulphoxide*, $(MeO\cdot C_6H_2Me_2)_2SO$, *and Sulphonium Base*, $(MeO\cdot C_6H_2Me_2)_3S\cdot$.—Sulphination as usual. The product was poured on broken ice, and, when the ensuing reaction had subsided, the mixture was extracted with chloroform. The sulphinic acid was removed from the chloroform solution by shaking with aqueous alkali carbonate, from which it was precipitated by the addition of mineral acid.

5-*Methoxy*-m-*xylene-2-sulphinic acid* crystallises from hot water in slender needles which melt at 94—95°. It is sparingly soluble in cold water and readily so in alcohol. The solution in concentrated sulphuric acid exhibits a characteristic violet colour :

0·1506 gave 0·2985 CO_2 and 0·0805 H_2O. C = 54·04 ; H = 5·93.

$C_9H_{12}O_3S$ requires C = 54·0 ; H = 6·0 per cent.

The original extract now contained sulphoxide together with a very small quantity of sulphonium chloride. The latter was separated by warming with water the residue left by evaporation of the chloroform. The sulphonium chloride crystallised from the cold aqueous solution in colourless needles, but the quantity furnished by this experiment was so small that a more complete examination of the substance was postponed until a further quantity had been obtained by another method. The viscous residue, now free from sulphonium chloride, was dried and then set aside in a vacuum, but it showed no tendency to crystallise until pure ether had been added. After the ethereal solution had remained about a week at the ordinary temperature, the crystalline precipitate of sulphoxide was collected and recrystallised from alcohol.

5-*Methoxy*-m-*xylyl sulphoxide* forms colourless, flat prisms which melt at 154—155°. It is moderately soluble in cold alcohol and very sparingly so in ether. The solution in concentrated sulphuric acid is violet :

0·1494 gave 0·1128 $BaSO_4$. S = 10·31.

$C_{18}H_{22}O_3S$ requires S = 10·06 per cent.

Ten grams of the phenolic ether yielded 3·5 grams of sulphinic acid, about 0·7 gram of the sulphoxide, and a very small quantity of the sulphonium chloride.

Action of Thionyl Chloride on m-5-*Xylenol Methyl Ether.*

A mixture of 10 grams of powdered aluminium chloride and an equal weight of phenolic ether was placed in a flask surrounded by ice. Five grams of thionyl chloride were then added, very slowly at first while the reaction was violent and more rapidly later. When shaken at intervals during the reaction, the mixture involved much hydrogen chloride. Finally, the deep violet product was set aside at the ordinary temperature for two hours and then decomposed in the usual way with powdered ice. The three products were isolated by the process which has already been described.

The yields of the products when compared with those obtained with sulphurous acid illustrate the stronger sulphinating powers of thionyl chloride. Only about half a gram of sulphinic acid was isolated, whilst the yield of crude sulphoxide was 6 grams, but this contained an oily impurity, probably sulphide. The amount of sulphonium chloride produced was also larger, 1 gram being formed by the sulphination of 10 grams of the ether.

tris-5-*Methoxy*-m-*xylyl*-2-*sulphonium chloride*, $(MeO\cdot C_6H_2Me_2)_3SCl$, crystallises from hot water in long, colourless needles, which melt at 103—105° and contain 7 molecules of water of crystallisation. A sample which had been dried in the air at the ordinary temperature was heated to 110° until constant weight was attained:

0·2597 lost, at 110°, 0·0540 H_2O. $H_2O = 20·79$.

0·1386 gave 0·0314 AgCl. Cl = 5·60.

$C_{27}H_{33}O_3ClS,7H_2O$ requires $H_2O = 21·05$; Cl = 5·93 per cent.

This sulphonium chloride dissolves with a violet-brown colour in concentrated sulphuric acid.

The *platinichloride* was obtained as an orange-coloured, crystalline powder melting at 160°:

0·1801 gave 0·3302 CO_2 and 0·0804 H_2O. C = 50·0; H = 4·96.

0·1244 „ 0·0192 Pt. Pt = 15·43.

$C_{54}H_{66}O_6Cl_6S_2Pt$ requires C = 50·54; H = 5·14; Pt = 15·21 per cent.

In conclusion, the authors wish to express their most hearty thanks to Professor Collie and to Dr. Stewart for their valuable criticism during the above experiments.

The Organic Chemistry Laboratory,
University College,
London.

ANNUAL GENERAL MEETING,

MARCH 26TH, 1908.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., in the Chair.

Dr. A. McKenzie and Dr. G. T. Morgan were appointed Scrutators, and the ballot was opened for the election of Officers and Council for the ensuing year.

The President presented the Report of the Council on the progress of the Society during the past twelve months, and the Treasurer gave a statement as to the Society's income and expenditure during the year 1907.

The adoption of the Report of the Council, together with the Balance Sheet and statements of Accounts for the year ended 31st December, 1907, was proposed by Professor A. LIVERSIDGE, seconded by Professor E. DIVERS, and carried unanimously.

A vote of thanks to the Auditors, which was proposed by Dr. ALEXANDER SCOTT, seconded by Mr. OTTO HEHNER, was acknowledged by Dr. H. FORSTER MORLEY.

REPORT OF THE COUNCIL.

As in recent years, the Council have the satisfaction of stating that the prosperity of the Society continues, both the number of papers read and the number of Fellows on the list showing a considerable increase.

On the 31st December, 1906, the number of Fellows was 2,860. During 1907, 137 Fellows were elected and 5 reinstated, making a gross total of 3,002. The Society has lost 30 Fellows by death; 30 have resigned; 1 election and 1 reinstatement have become void; 1 newly-elected Fellow has withdrawn, and the names of 43 Fellows have been removed from the list for non-payment of Annual Subscriptions.

The total number of Fellows, therefore, at the 31st December, 1907, was 2,896, showing an increase of 36 over the number for the previous year.

The names of the deceased Fellows, with the dates of their election, are:

A. C. Aitkin (1901).
T. Andrews (1870).
P. T. Austen (1877).
A. Bottle (1873).
W. Bowen (1903).
E. Chapman (1868).
E. D. Chester (1882).
J. Clark (1876).
George Davey (1893).
A. Dupré (1860).
J. Gale (1866).
Sir D. Gamble, Bart. (1851).
S. Hall (1876).
L. F. V. Harcourt (1863).
B. J. Harrington (1897).
J. Ince (1867).
F. Keeling (1883).
C. O'Sullivan (1876).
F. J. M. Page (1871).
A. C. Palmer (1906).
S. Parfitt (1906).
Sir W. H. Perkin (1856).
H. D. Perkins (1905).
B. C. Polkinghorne (1899).
W. Pritchard (1870).
R. R. Swann (1905).
J. F. Walker (1865).
R. Warington (1863).
H. A. Wetzel (1883).
H. E. Wright (1900).

The following Fellows have resigned:

A. Amos.
A. C. Benson.
T. H. Boardman.
J. Cameron.
J. Daniell.
T. Divine.
G. Dyson.
A. T. Eutroppe.
J. A. Fawcett.
G. Goldfinch.
W. F. Grace.
R. Grimwood.
W. B. Hards.
G. H. U. Harrow.
H. J. Hodges.
W. A. F. Lethbridge.
H. Martin.
H. G. F. Micklewright.
J. T. Nance.
D. Northall-Laurie.
A. N. Palmer.
E. W. Sawdon.
T. Steel.
S. D. Stennitt.
A. E. Tanner.
W. H. Templeman.
J. H. Wainwright.
J. W. Wells.
H. Wilson.
J. H. Wolfenden.

The number of those Fellows who were elected prior to 1860 has been still further diminished by the death of Sir David Gamble, Bart., who was elected on March 17th, 1851, and Sir William H. Perkin, who was elected on December 15th, 1856.

The number of Honorary and Foreign Members at the close of 1906 was 33. No elections have taken place during 1907, but the Society has to mourn the loss of Professor Marcellin Berthelot, elected March 1st, 1860, deceased March 18th; Professor Dr. Dmitri Ivanovitsch Mendeléeff, elected February 1st, 1883, deceased February 2nd; Professor Dr. Nicolai Menschutkin, elected January 20th, 1898, deceased February 5th; and Professor Henri Moissan, elected January 20th, 1898, deceased February 20th. The number of Honorary and Foreign Members, therefore, at the 31st December, 1907, was 29.

During the year 1907, 268 scientific communications have been made to the Society, 203 of which have been published already in the *Transactions*, and abstracts of all have appeared in the *Proceedings*.

The volume of Transactions for 1907 contains 2,089 pages, of which 2,021 are occupied by 205 memoirs, the remaining 68 pages being devoted to the Faraday Lecture, the Obituary Notices, the Report of the Annual General Meeting, and the Presidential Address; the volume for the preceding year contains 186 memoirs, which occupy 1,890 pages.

The Journal for 1907 contains also 4,686 abstracts of papers published mainly in foreign journals, which extend to 2,100 pages, whilst the abstracts for 1906 numbered 4,541, and occupied 1,912 pages.

The abstracts for 1907 may be classified as follows:

	Pages.	No. of Abstracts.
PART I.		
Organic Chemistry	1,104	1,831
PART II.		
General and Physical Chemistry		725
Inorganic Chemistry		622
Mineralogical Chemistry		117
Physiological Chemistry		545
Chemistry of Vegetable Physiology and Agriculture		244
Analytical Chemistry		602
	996	2,855
Total in Parts I. and II.	2,100	4,686

In the hope of diminishing the confusion which had arisen in the nomenclature of the proteins, consideration of the subject was undertaken by the Publication Committee, in conjunction with representatives of the Physiological Society; the joint committee concluded their deliberations early in 1907, and their recommendations appear in the Proceedings for that year.

Recognising the importance, from a public standpoint, of the Presidential Address delivered by Professor Meldola, F.R.S., in March, 1907, the Council have felt it desirable that his remarks on that occasion should attract the attention of a wider circle than is reached by the Society's Transactions; accordingly 5,000 copies of the address have been circulated among the members of various public bodies, including both Houses of Parliament, and the Council hope that this unusual step will have the effect of bringing the subject of Professor Meldola's discourse into suitable prominence.

During the past year, the Society has had to mourn the loss of Sir William Perkin, which took place on July 14th, 1907, just twelve months after the International Celebration which marked the Fiftieth Anniversary of the Foundation of the Coal Tar Colour Industry. This is not the place in which to deal with the splendid achievements of the late Past President, or the qualities which endeared him to the Fellows, who will remember with melancholy satisfaction that he lived to participate in the widely-supported public appreciation of the preceding year, and in the subsequent commemoration celebrated in the United States. The marble bust of Sir William Perkin has now been placed in the meeting room, and a large photograph of the portrait painted by Mr. A. S. Cope, A.R.A., is also the property of the Society, having been presented by Sir William a few months before his death.

In view of the losses incurred during recent years through the death of several Honorary and Foreign Members, thereby reducing the number of survivors to 29, the Council recommended for election the following distinguished chemists: Professor A. E. J. Gautier, Professor Albin Haller, Professor J. W. Hittorf, Professor J. A. Le Bel, Professor H. L. Le Chatelier, Professor T. W. Richards, and Professor Otto Wallach. This recommendation was duly ratified by the Society at the meeting on Thursday, February 6th, 1908.

An agreeable feature of the past year has been the Jubilee Celebration of the Société Chimique de France, and on that occasion an address of congratulation was presented by Sir William Ramsay, F.R.S., on behalf of the Society, which was represented also by Professor H. E. Armstrong, F.R.S., and Dr. Horace Brown, F.R.S.; a commemorative medal has been received from the French institution, and added to the Society's collection. A somewhat similar event took place in September, when the Geological Society celebrated their Centenary, the President being again delegated to offer the felicitations of the Chemical Society. A copy of the recently compiled History of the Geological Society has been since presented to the Library.

Professor J. Bretland Farmer, F.R.S., accepted the invitation of the Council to deliver a discourse before the Society, and his lecture, entitled "Some Borderline Problems in Botany," was greatly appreciated by the Fellows.

Late in 1906, Geheimrat Professor Emil Fischer, F.R.S., an Honorary and Foreign Member since 1892, was nominated Faraday Lecturer, and gave his address, in German, on October 18th, 1907, in the theatre of the Royal Institution, kindly lent by the managers for the occasion; at the termination of the lecture, entitled "Synthetical Chemistry in its Relation to Biology," the Faraday Medal was presented to Professor Fischer by the President.

In common with all corporate bodies engaged in scientific pursuits, the Chemical Society has keenly deplored the death of Lord Kelvin, who, although not on the roll of Fellows, had been the guest of the Society on many occasions. At the request of the Council, the President transmitted to Lady Kelvin a resolution of sympathy, and the Society was represented at the funeral ceremony in Westminster Abbey.

Professor W. Wislicenus, of Tübingen, having initiated a memorial to the late Professor Lothar Meyer, the Treasurer was authorised to contribute from the funds of the Society, and the Council venture to hope that the memorial may be supported by individual Fellows.

The ventilation of the meeting room and council chamber has occupied the attention of the House Committee, who have recommended the installation of electric fans; since their report was received and adopted by the Council, a Fellow who desires to remain anonymous, has most kindly undertaken to defray the cost of this highly necessary improvement.

In addition to an engraving of Daniell and Faraday, for which the Society is indebted to Professor Meldola, F.R.S., numerous articles of historical interest and value have come into the possession of the Society in virtue of a bequest by the late Professor Warington.

The number of books borrowed from the Library during 1907 was 1,317, as against 1,126 in the previous year. The additions to the Library comprise 138 books, of which 79 were presented, 401 volumes of periodicals (representing 243 journals), and 40 pamphlets, as against 121 books, 385 volumes of periodicals (representing 229 journals), and 32 pamphlets last year.

The experiment of opening the Library during Thursday evenings other than those on which the Society meets has been discontinued, so few Fellows having used the Library on those occasions.

In May, 1907, a special leaflet was issued with the Journal indicating the parts required to complete certain sets of periodicals in the Library, in the hope that Fellows happening to possess copies of the desired numbers would present them to the Society. In response to that circular, donations were received from numerous Fellows, and this favourable response has encouraged the Council to hope that further contributions of a similar character may be added to the Library.

As was announced at the last Annual Meeting, the Society received from the Worshipful Company of Goldsmiths a munificent donation of £1,000 for the Research Fund. This fund has been still further increased by the handsome sum of £2,704 3*s*. 8*d*., which was handed over to the Treasurer in July by the Perkin Memorial Fund Committee. These two sums, as now invested, have augmented the annual income of the Research Fund by £126 5*s*., and will enable the Research Fund Committee in the present year to recommend the Council to make grants to the amount of £340 to £350. Of this sum, about £34 is more or less especially to be devoted to the encouragement of research in inorganic and metallurgical chemistry, and about £92 for investigations relating to problems connected with the coal-tar and allied industries.

In spite of several items of a somewhat exceptional nature, the Treasurer is glad to be able to report that he has a substantial surplus to carry forward as the result of the year's finance. The income of the Society from all sources for 1907 is £7,260 4*s*. 10*d*., as against £7,121 8*s*. 11*d*. in 1906, and the expenditure is £6,750 8*s*. 5*d*., instead of £6,379 15*s*. 9*d*., so that, whilst our expenditure has increased by £370 12*s*. 8*d*., our income has only grown by £138 15*s*. 11*d*. This still leaves a surplus of £509 16*s*. 5*d*. on the year's working.

The increase in income may be put down almost entirely to the increase in Annual Subscriptions, for the increase of £100 in the Life Compositions is more than neutralised by the drop of £104 in Admission Fees.

The *Journal* and *Annual Reports* have cost respectively £182 19*s*. 8*d*. and £24 8*s*. 5*d*. more than last year, but a saving of £23 18*s*. has been effected on the *Proceedings* and the *List of Fellows*. The reprinting of certain numbers of the *Proceedings* which were "out of print" has put it within the power of Fellows to complete their sets of *Proceedings*, and the increase in the sale has already more than repaid the cost of the reprints.

A certain amount of redecoration beyond the annual cleaning, the balance of the Dinner account, and the printing and distribution of 5,000 copies of last year's Presidential Address are the chief items which have raised the "administrative expenses" so much above those of last year.

In July the Treasurer was able to purchase £1,200 North British Railway 3 per cent. Debenture Stock; a glance at the balance sheet will show that the value of the invested capital of the Society was on December 31st, 1907, £18,362 9*s*. 9*d*., and that of the Research Fund, £10,016 11*s*. 10*d*.

BALANCE SHEET.—THE CHEMICAL SOCIETY, 31st December, 1907.

Liabilities.

	£	s.	d.	£	s.	d.
To Subscriptions received in advance				229	0	0
,, Cash received on Account of Annual Report, Vol. IV. (not published)				20	3	0
,, Sundry Creditors				1398	19	6
,, Research Fund:—						
As per last Balance Sheet	6817	18	6			
Add Grant from Goldsmiths' Company	1000	0	0			
,, Balance of Perkin Memorial Fund	2704	3	8			
,, Excess of Income over Expenditure for the year	8	19	10			
				10530	17	0
,, Chemical Society:—						
As per last Balance Sheet	19135	13	3			
Add Excess of Income over Expenditure for the year	509	16	5			
				19645	9	8
				£31824	9	2

Assets.

	£	s.	d.	£	s.	d.
By Investments (value when acquired):—						
£1050 London and North Western Railway 3 per cent. Debenture Stock	889	12	0			
£6730 Metropolitan Consolidated 3½ per cent. Stock	7212	8	6			
£1529 14*s*. 3*d*. Cardiff Corporation 3 per cent. Stock	1650	0	0			
£1400 India 2½ per cent. Stock	1316	1	0			
£2400 Bristol Corporation 2½ per cent. Debenture Stock	2070	2	0			
£4341 Midland Railway 2½ per cent. Preference Stock	3572	2	5			
£1200 Leeds Corporation 3 per cent. Stock	1143	1	0			
£1500 Transvaal 3 per cent. Guaranteed Stock	1460	13	6			
£1200 North British Railway 3 per cent. Debenture Stock	1033	11	0			
				20207	11	5
(Estimated present value of Investments, £18362 9*s*. 9*d*.)						
,, Library, Furniture, Stock of Publications, &c. (not valued)						
,, Sundry Debtors:—						
Society of Public Analysts	12	12	0			
Advertising Agents	50	0	11			
Messrs. Gurney & Jackson	471	16	3			
Telephone Deposit	1	0	0			
				535	9	2
,, Subscriptions in Arrear, £416. Estimated to realise				280	0	0
,, Insurance paid in advance				17	2	9
,, Cash at Bank	152	14	5			
,, ,, in hand	10	14	5			
				163	8	10
,, Research Fund:—						
Investments (value when acquired):						
£1000 North British Railway 4 per cent. No. 1 Preference Stock	1010	0	0			
£4400 Metropolitan Consolidated 3½ per cent. Stock	4587	18	0			
£1034 Great Western Railway 2½ per cent. Debenture Stock	1049	15	11			
£1142 16*s*. New South Wales 3 per cent. Stock	1000	0	0			
£1122 Metropolitan Water Board 3 per cent. "B" Stock	1002	16	9			
£1365 Midland Railway 2½ per cent. Debenture Stock	1010	0	9			
£806 Victoria 3 per cent. Stock	706	6	2			
	10366	17	7			
(Estimated present value of Research Fund Investments, £10016 11*s*. 10*d*.)						
Cash at Bank	163	19	5			
				10530	17	0
				£31824	9	2

INCOME AND EXPENDITURE ACCOUNT

Income.

		£	s.	d.	£	s.	d.
To Life Compositions					368	0	0
,, Admission Fees					608	0	0
,, Annual Subscriptions—							
Received in advance, on account of 1907		237	0	0			
,, during 1907 ,, 1907		4064	0	0			
,, ,, ,, ,, 1906		296	2	0			
,, ,, ,, ,, 1905		2	0	0			
		4599	2	0			
Less amount included in last year's Income, being valuation of Arrears as per last Balance Sheet		260	0	0			
		4339	2	0			
Add Arrears to date: 1907 £384, 1906 £24, 1905 £8, estimated to realise as per Balance Sheet		280	0	0	4619	2	0
,, Investments :—							
Dividends on £6730 Metropolitan Consolidated 3½ per cent. Stock ...		223	15	6			
,, £1050 London and North Western Railway 3 per cent. Debenture Stock		29	18	6			
,, £1520 14*s.* 3*d.* Cardiff Corporation 3 per cent. Stock ...		43	6	8			
,, £1400 India 2½ per cent. Stock		33	5	0			
,, £2400 Bristol Corporation 2½ per cent. Debenture Stock		57	0	0			
,, £4341 Midland Railway 2½ per cent. Preference Stock		103	2	0			
,, £1200 Leeds Corporation 3 per cent. Stock		34	4	0			
,, £1500 Transvaal 3 per cent Guaranteed Stock		42	15	0			
,, £1200 North British Railway 3 per cent. Debenture Stock		17	2	0			
Income Tax Recovered		29	17	0			
Interest on Deposit Account		29	9	8	642	15	1
Publications :—							
Sales :							
Journals		847	15	11			
Proceedings		38	9	7			
General Index		20	2	6			
Memorial Lectures		6	15	0			
Library Catalogue		1	14	9			
Atomic Weight Tables			18	10			
Annual Reports on the Progress of Chemistry		133	19	0			
		1049	15	7			
Less Publishers' Commission		100	9	9			
		949	5	10			
Proceeds of Advertisements in Journal...	£58 17 6						
Less Commission	8 16 7						
		50	0	11	999	6	9
,, Subscriptions from other Societies :—							
Society of Chemical Industry		9	9	0			
Society of Public Analysts		12	12	0	22	1	0
					£7260	4	10

I have examined the above Accounts with the Books and Vouchers of the Society, and and the Investments.

9th March, 1908.

W. B. KEEN,
Chartered Accountant.

FOR THE YEAR ENDED 31ST DECEMBER, 1907.

Expenditure.

	£	s.	d.	£	s.	d.
By Expenses on account of Journal and Proceedings:—						
Salary of Editor	300	0	0			
Salary of Sub-Editor	200	0	0			
Salary of Assistant Sub-Editor	60	0	0			
Salary of Indexer and Assistance	97	0	0			
Editorial Postages, &c.	21	14	3			
Abstractors' Fees	497	3	5			
Printing of Journal	2460	12	1			
Printing of Advertisements	31	6	9			
Distribution of Journal	506	3	3			
Printing of Wrappers and Addressing	119	3	7			
Authors' Copies	133	3	0			
Insurance of Stock at Clay's	10	3	0			
				4436	9	4
Printing of Proceedings	215	19	8			
Distribution of Proceedings	59	11	10			
				275	11	6
,, Annual Reports on the Progress of Chemistry				538	18	6
,, Reprints of back numbers of Proceedings				17	3	0
,, Purchase of back numbers of Journal				13	19	11
,, List of Fellows				71	14	0
,, Library Expenses:—						
Salary of Librarian	120	0	0			
Books and Periodicals	195	11	11			
Binding	45	14	6			
				361	6	5
,, Indexing for International Catalogue				30	0	0
,, Faraday Lecture:— Honorarium and Expenses				30	7	2
,, Administrative Expenses:—						
Salary of Assistant Secretary	190	0	0			
Salary of Office Assistant	32	10	0			
Wages (Commissionaire, Housekeeper, and Charwoman)	152	11	0			
Pension, Mrs. Hall	30	0	0			
Coal and Lighting	41	19	8			
Decorative Work	62	8	9			
House Expenses and Repairs	59	1	9			
Tea Expenses	31	11	0			
Insurance	10	6	8			
Accountants' Charges	10	10	0			
Accountants' Commission on Recovery of Income Tax	1	9	10			
Audit Fee:— Perkin Memorial Fund	2	2	0			
Miscellaneous Printing	125	3	5			
Stationery	50	15	5			
Postages	116	4	11			
Balance of Dinner Account	30	2	9			
Miscellaneous Expenses	28	1	5			
				974	18	7
,, Balance, being excess of Income over Expenditure, carried to Balance Sheet				500	16	5
				£7260	4	10

certify them to be in accordance therewith. I have also verified the Balance at the Bankers

Approved— Hy. Forster Morley,
Arthur Harden,
J. Augustus Voelcker.

Research Fund Income and Expenditure Account for the Year ended 31st December, 1907.

Income.

	£	s.	d.	£	s.	d.
To Dividends on :—						
£1000 North British Railway 4 per cent. Stock	38	0	0			
£4400 Metropolitan Consolidated 3½ per cent. Stock	146	6	0			
£1034 Great Western Railway 2½ per cent. Debenture Stock	24	11	2			
£1122 Metropolitan Water Board 3 per cent. "B" Stock	15	19	10			
£1142 16s. New South Wales 3 per cent. Stock	16	5	9			
Interest on Deposit Account	10	8	11			
				251	11	8
,, Repayment of Research Grants :—						
F. G. Donnan	1	19	0			
F. C. Garrott and J. A. Smythe	7	1	6			
J. N. Collie	2	7	2			
A. E. Dunstan		5	4			
H. Henstock	4	6	7			
W. B. Tuck		2	2			
A. Lapworth		5	8			
J. Hawthorne		12	6			
W. H. Mills	2	0	5			
A. G. Perkin		7	0			
				19	7	4
,, Income Tax Recovered				10	19	10
				£281	18	10

Expenditure.

	£	s.	d.	£	s.	d.
By Grants to—						
E. C. C. Baly	20	0	0			
A. T. Cameron	10	0	0			
A. E. Dunstan	5	0	0			
C. E. Fawsitt	5	0	0			
Miss A. Homer	5	0	0			
T. M. Lowry	10	0	0			
T. S. Moore	5	0	0			
R. H. Pickard	5	0	0			
C. Smith	5	0	0			
J. J. Sudborough	20	0	0			
W. B. Tuck	12	0	0			
E. A. Werner	10	0	0			
G. Young	10	0	0			
J. A. Carpenter	25	0	0			
K. Fisher	15	0	0			
W. N. Haworth	15	0	0			
A. N. Meldrum	15	0	0			
R. Robinson	20	0	0			
J. L. Simonsen	20	0	0			
A. W. Stewart	10	0	0			
V. H. Veley	15	0	0			
H. Watson	15	0	0			
				272	0	0
,, Commission on Recovery of Income Tax					11	0
,, Cheque Book					8	0
,, Balance, being excess of Income over Expenditure, carried to Balance Sheet				8	19	10
				£281	18	10

I have examined the above Account with the Books and Vouchers of the Society, and certify it to be in accordance therewith. have also verified the Balance at the Bankers and the Investments.

W. B. Keen,
Chartered Accountant.

9th March, 1908.

Approved— Hy. Forster Morley,
Arthur Harden,
J. Augustus Voelcker.

A vote of thanks to the Treasurer, Secretaries, Foreign Secretary, and Council for their services during the past year was proposed by Dr. **Frank Clowes**, seconded by Dr. **W. E. Adeney**, and unanimously adopted. Professor J. **Emerson Reynolds** responded.

The **President** then delivered his Address, which will be found on p. 774.

Professor **Raphael Meldola** proposed a vote of thanks to the President for his address and for his services in the Chair during the past year, coupled with the request that he would allow the address to be printed in the *Transactions* of the Society. Dr. **Rudolph Messel** seconded the motion, which was put to the Meeting and carried with acclamation.

The Report of the Scrutators was presented to the President, who declared the following to have been elected as Officers and Council for the ensuing year:

President: Sir William Ramsay, K.C.B., F.R.S.

Vice-Presidents who have filled the Office of President: H. E. Armstrong, Ph.D., LL.D., F.R.S.; A. Crum Brown, D.Sc., LL.D., F.R.S.; Sir William Crookes, D.Sc., F.R.S.; Sir James Dewar, M.A., LL.D., F.R.S.; A. G. Vernon Harcourt, M.A., D.C.L., F.R.S.; Raphael Meldola, F.R.S.; H. Müller, Ph.D., LL.D., F.R.S.; W. Odling, M.A., M.B., F.R.S.; J. Emerson Reynolds, Sc.D., M.D., F.R.S.; Sir Henry E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; T. E. Thorpe, C.B., LL.D., F.R.S.; W. A. Tilden, D.Sc., F.R.S.

Vice-Presidents: J. Campbell Brown, D.Sc., LL.D.; J. J. Dobbie, M.A., D.Sc., F.R.S.; F. Stanley Kipping, D.Sc., Ph.D., F.R.S.; Rudolph Messel, Ph.D.; Sir Alexander Pedler, C.I.E., F.R.S.; W. H. Perkin, Ph.D., F.R.S.

Treasurer: Alexander Scott, M.A., D.Sc., F.R.S.

Secretaries: M. O. Forster, D.Sc., Ph.D., F.R.S.; A. W. Crossley, D.Sc., Ph.D., F.R.S.

Foreign Secretary: Horace T. Brown, LL.D., F.R.S.

Ordinary Members of Council: Julian L. Baker; George T. Beilby, F.R.S.; Alfred C. Chapman; Julius B. Cohen, Ph.D., B.Sc.; J. T. Hewitt, M.A., D.Sc., Ph.D.; W. R. E. Hodgkinson, Ph.D.; H. A. D. Jowett, D.Sc.; H. R. Le Sueur, D.Sc.; F. E. Matthews, Ph.D.; A. G. Perkin, F.R.S.; W. J. Sell, Sc.D., F.R.S.; John Wade, D.Sc.

PRESIDENTIAL ADDRESS.

Delivered at the ANNUAL GENERAL MEETING, March 26th, 1908.

By Sir WILLIAM RAMSAY, K.C.B., F.R.S.

The Electron as an Element.

> "Nec perit in toto quicquam, mihi credite, mundo,
> Sed variat faciemque novat."—OVID.

BEFORE commencing my task, to attempt to show that chemical phenomena may be represented in a reasonable manner by assigning a symbol to the electron, considered as an element, it will be advisable to make some general statements regarding the relations between thinking man and external nature.

Every one of us (and by "us" I mean to include all things which have, even in embryo, consciousness both of their own existence and that of objects external to them) holds certain suppositions, whether by inheritance or by early teaching, or by virtue of having formed his own deliberate judgment, to be true; or if the word true be found objectionable, to be convenient; to be necessary as a mode of thought. Such suppositions we term theories or hypotheses. These words themselves require definition. To quote Dr. Johnstone Stoney: "The principal kinds of supposition are: Theories, Hypotheses, and Fictions. A theory means a supposition which we hope to be true; a hypothesis is a supposition which we expect to be useful. Fictions belong to the realm of art; when allowed to intrude elsewhere, they become either Make-believes or Mistakes."

Chemists and physicists deal with the world of phenomena; with operations and results of operations which take place in what is called "nature," that is, in a region exterior to the minds of the observers. They have agreed, implicitly, to avoid the consideration of the relationship between such phenomena and the mind of man, a branch of the subject termed Metaphysics; they confine their attention exclusively to the relationships which they observe to exist between various phenomena external to the workings of consciousness. It is true that all such phenomena are known to us only in so far as they impress our consciousness—our own minds, or the minds of other beings whom each of us regards as constituted more or less nearly like himself. But inasmuch as there is a consensus of opinion, on the whole, as to the similarity of impression received by conscious beings, we agree to ignore the inquiry as to the mode in which such impressions reach our minds and to confine our attention to the relationships which we find to exist among phenomena.

Now, there are two ways of regarding natural phenomena, and these necessarily depend on the fundamental conceptions which all of us hold. We assume, first, that events happen in sequence, and from this we deduce the conception of time. Secondly, we believe that we can change our position relatively to that of other objects, and that they change their relative position to each other; we thus acquire the conception of space. Whether these ideas are engrained from birth, or acquired by experiment or observation, we shall probably never know. Thirdly, we are conscious of sustained muscular effort, and from this consciousness we deduce two ideas, first, that of mass, or that which resists our muscular efforts; and second, that of energy, or, in other words, we learn that to change the position of an object or mass, a sustained muscular effort is necessary. This last conception is of recent introduction; the word, I believe, used in this sense, was due to Professor Macquorne Rankine.

If we assign certain numerical values to these conceptions, if we measure time in seconds, linear space in centimetres, and mass in grams, we arrive at a fundamental equation connecting these with energy, measured in ergs. It is the familiar one:

$$E = \tfrac{1}{2}ML^2/T^2,$$

where E, L, M, and T may stand for equal number of ergs, grams, centimetres, and seconds respectively.

It will be observed that only three of these fundamental notions are necessary; the fourth can be deduced from the other three. Physicists and chemists have for centuries accepted time, space, and mass as fundamentals, and have agreed to derive the conception of energy from these three. That is, they have accepted a mechanical explanation of the universe; they attempt to explain the invisibly minute in terms of the visible; the nature of objects by the atomic and molecular theories, namely, by the supposition that objects consist of congeries of small masses; that the changes which they observe to occur in these objects are due to the motions and altered positions of the atoms and molecules, and that the nature of these objects depends largely on the relative positions of the atoms, or, as we say, on their structure. It is, of course, acknowledged that the changes that take place in objects are accompanied by gain or loss of energy. To alter the position of a mass, energy must be imparted to it, or, if it spontaneously alter its position, it must part with energy in doing so.

The whole conception of a "material universe" is bound up in this view, which has contributed to a great advance in knowledge; in fact, all progress in chemistry and physics has been made by its aid. The atomic theory is a "theory," a supposition which is supposed to be true, as well as a "hypothesis," which is known to be useful. By its help we "explain" (that is, render the unknown in terms of the more familiar) such apparently diverse facts as the relations between the volume, temperature, and pressure of gases; the optical properties of certain compounds of carbon, nitrogen, sulphur, tin, and silicon; isomerism; the phenomena of osmotic pressure and vapour pressure; and with an added hypothesis, the behaviour of dissolved salts under electric stress. It is this last part of our conceptions which I propose to discuss in this address.

But before proceeding to do so, it must be noticed that it is possible to explain phenomena by postulating time, space, and energy as the three fundamentals; mass is then a derived conception. To my mind, this method of viewing nature is the more logical, for all that we know through our senses directly, and indirectly by instruments which affect our senses, is due to transfer of energy to or from our nerve-terminals. Such sensations are for us real; in ascribing them to the presence of "matter" as their cause, we make use of a theory which is sanctioned by antiquity, and by all but universal custom. The inconvenience of the hypothesis that energy is the third fundamental entity is that it is difficult to assimilate mentally, and that it results in sets of equations of state, instead of affording a mental picture of the minute unknown in terms of the larger, and better known. Those interested in the subject will find it expounded in various writings of Prof. Mach and of Prof. Ostwald, notably in the latter's "Naturphilosophie."

I should like here to pause, and to note that the words "true" and "*false*" are inapplicable to such theories as these of which I have spoken. Both are perfectly consistent schemes for the interpretation of the universe. In all probability, neither of these schemes conveys any idea of what constitutes phenomena; one or other may be regarded as more *convenient*. Let me here refer to Dr. Johnstone Stoney's writings for a full discussion of such relations.*

As a matter of convenience, then, like most other chemists and physicists, I choose deliberately the "mechanical" explanation of nature. We assume on what we consider to be good grounds the existence of molecules and of atoms. We believe on reasonable evidence that gases consist of almost innumerable molecules, which may, like argon and its congeners, be single atoms, but which are usually groups of atoms. We hold that, as a rule, liquids consist of molecules of the same order of complexity as gases, but with smaller free path; the molecules of a liquid are more crowded than those of a gas. Some few liquids, water, the alcohols, the acids, probably salts, and some others, may be regarded as mixtures of polymerides of their gaseous molecules. Of the structure of solids, we are only beginning to have some crude notion.*

---

* "On the dependance of what apparently takes place in nature upon what actually occurs in the universe of real existences."—*Amer. Philosoph. Soc.*, Vol. XLII, No. 173. "On the relation between natural science and ontology."—*Sci. Trans. Roy. Dubl. Soc.*, Vol. VI, Part 9.

We also believe that molecules at the ordinary temperature are in enormously rapid motion; that they are in frequent collision with each other, and that chemical action is the occasional result of such collisions. I say "occasional" because, as Dr. Stoney has shown, in molecules such as those of the nitrogen and oxygen of air, a collision takes place on the average thirteen billion times every second. Some mixtures of gases, for example, hydrogen and oxygen, or hydrogen and chlorine, at a suitable temperature, combine by virtue of such collisions between the molecules; but the process of combination is a comparatively slow one, and it is curious to think that a collision which is followed by a combination is a comparatively rare event. "We begin to perceive that chemical reactions, even those that occur with explosive violence, are far from being the sudden events they seem to ordinary human apprehension. What is really occurring in nature is a *protracted* and eventful struggle between the members of two opposing armies, each individual unit of which has his own personal history during the struggle, and is fully occupied with his own acts, which are perhaps, as many, as various, and as different from those of his neighbours as are the thoughts and acts of the individual soldiers during the progress of a battle." †

What is meant by "chemical action"? We can represent it as a loss or gain of energy, but we also regard it as the union or junction of atoms, or, it may be, the dissolution of such union or the re-adjustment of unions, so that bodies with new properties are formed. We may next ask: What mechanism can be devised to give us a picture of the union of two atoms? Do they interpenetrate? Are atoms vortex-rings, and is their union the annular revolution of the two rings? Or is the older conception to be preferred, that they are approximate spheres which come within and stay within the regions of each others' influence? If so, why do they stay near each other? Various chemists have called the mechanism by which it is conceived that atoms remain associated in a compound "affinities" or "bonds," and "valency" is a word used to express the number of such "bonds" which an element can exercise in any particular combination.

I have to bring before you a suggestion which, although not exactly new, admits of definite statement, and affords a mental picture of what may conceivably takes place. It is not a "theory"; I do not hope that it may be true; it is rather a hypothesis, a supposition that I expect to be useful; it may be a "make-believe"; I trust that it will not be a "mistake."

---

* "Texture in media."—*Phil. Mag.*, June, 1890.

† Dr. Stoney, "Survey of that part of nature which man is competent to study." —*Phil. Mag.*, Nov., 1899.

The hypothesis admits of short statement. It is: electrons are atoms of the chemical element, electricity; they possess mass; they form compounds with other elements; they are known in the free state, that is, as molecules; they serve as the "bonds of union" between atom and atom. The electron may be assigned the symbol "E."

I might begin the exposition of this subject with a historical sketch of Davy's and Berzelius's conceptions of the relations of chemical and electrical phenomena; it will suffice for my purpose to direct your attention to the Faraday lecture delivered before our Society in 1881. Professor Helmholtz there stated: ". . . We need not speculate about the real nature of that which we call a quantity of positive or negative electricity. Calling them substances of opposite sign, we imply with this name nothing else than the fact that a positive quantity never appears or vanishes without an equal negative quantity appearing or vanishing at the same time in the immediate neighbourhood. In this respect they behave really as if they were two substances, which cannot be either generated or destroyed, but which can be neutralised and become imperceptible by their union." ". . . I prefer the dualistic theory. . . . and I keep the well-known supposition that as much negative electricity enters where positive goes away, because we are not acquainted with any phenomena which could be interpreted as corresponding with an increase or diminution of the total electricity contained in any body." Later in his lecture, discussing Faraday's law, he goes on: "The same definite quantity of either positive or negative electricity moves always with each univalent ion, or with every unit of affinity of a multivalent ion, and accompanies it during all its motions through the interior of the electrolytic fluid. This quantity we may call the electric charge of the ion." It is what Dr. Stoney has named an "electron." Helmholtz proceeds: "Now the most startling result of Faraday's law is perhaps this. If we accept the hypothesis that elementary substances are composed of atoms, we cannot avoid concluding that electricity also, positive as well as negative, is divided into definite elementary portions, which behave like atoms of electricity. As long as it moves about in the electrolytic liquid, each ion remains united with its electric equivalent or equivalents. At the surface of the electrodes, decomposition can take place if there is sufficient electromotive force, and then the ions give off their electric charges and become electrically neutral." I will make only one more quotation from Helmholtz. Dealing with "atomic compounds," that is, molecules consisting of atoms in union with each other, he said: "If we conclude from the facts that every unit of affinity is charged with one equivalent either of positive or negative electricity, they can form compounds only if every unit charged positively unites under the influence of a mighty electric attraction with another unit charged negatively. This, as you will immediately see, is the modern chemical theory of quantivalence, comprising all the saturated compounds."

Just twenty years later, in a lecture delivered at Hamburg in 1901, Professor Nernst again emphasised Helmholtz's views in the words: "If, further, the most different elements or radicles invariably combine only with a quite definite quantity of free electricity, or with a multiple thereof, this can be most simply expressed by the statement: for compounds between ordinary matter and electricity, exactly the same fundamental chemical law holds as for compounds with each other of ordinary chemical substances, namely, the law of constant and multiple proportions." "For example, if, in common salt, we replace the sodium atom by a negative electron, we obtain the negative chlorion; if we replace the chlorine atom by a positively charged electron, we obtain the positive sodium ion."

Helmholtz, it will be noticed, declared his assent to the dual character of electricity; Nernst has followed his example, and that view has, until of late years, been universally held. But it is well to remember that Benjamin Franklin attributed the action of electricity to a single "electrical fluid" residing in all bodies, and capable of passing from one to another. The particles of this fluid were supposed to repel one another, and to be attracted by the particles of ponderable matter. A positive electrified body was imagined by him to be one which had a surplus of electric fluid attached to it; a negatively electrified one, a deficit. This theory of Franklin's, *mutatis mutandis*, has gained probability since the investigations of J. J. Thomson, and since the discovery of radioactive bodies. It has been shown that electric corpuscles or electrons are capable of detaching themselves from matter, and inhabiting space unattached to any object. They pass from one part of space to another, often with enormous velocity. On certain likely suppositions, the mass of an electron has been measured by Thomson and his pupils; it does not differ much from the thousandth part of that of an atom of hydrogen. The electron may be termed an atom of negative electricity. The atom which it has left is generally, and by many supposed to be always, positively electrified. The mass of an atom from which one or more electrons have escaped does not differ appreciably from that of the atom of the element; it is enormously greater than that of the negative electron.

As may be supposed, such minute corpuscles find ordinary matter so coarse-grained, that in thin sheets it offers little resistance to penetration. The β-rays (to give electrons a commonly-used synonym) pass, when in motion, through a considerable thickness of metals and of glass. This behaviour is not unknown in the case of helium, which can traverse thin walls of silica, impervious to other gases, whilst glass and metals are impervious to it.

We are not here concerned with free electrons and their motions, but with the mode in which they are associated with matter; to render the conceptions clear, I will select a familiar instance.

When the white, opaque, lustrous metal sodium burns in the yellow gas chlorine, small, white, transparent crystals of common salt are produced. These crystals are soluble in water, the solution is also transparent and colourless, and its properties do not materially differ from those of the mean of salt and water. The power possessed by the solution of retarding the passage of light is very nearly proportional to the powers of the salt and the water, taken in the proportion in which they occur in solution. The specific heat of the solution, and many other properties, are also mean properties. What mechanism can we assign to the change which occurs when sodium burns in chlorine? When salt is dissolved in water and a "current of electricity" is passed through the solution, that is, when two platinum plates, one kept negatively and the other kept positively charged, are dipped into it, sodium travels towards the negative plate, and would, were no secondary action to occur, deposit in its original metallic state; similarly, chlorine would be liberated at the positive plate. We say that the salt is "ionised in solution," and we believe that the sodium ion remains an ion because of the positive charge which it carries, and, similarly, the properties of the chlorine ion are due to its negative charge. On removing these charges, the "elements" as we know them are liberated as such.

Now, I would argue that in the light of modern knowledge we must suppose that the terms "positive" and "negative" mean merely "minus electrons" and "plus electrons"; that the sodium ion or "sodion" is an element; that the metal sodium is a compound of the element "sodion" with an electron; that the chlorine ion is a compound of an electron (actually of more than one electron; see below) with an atom of chlorine.

It will conduce to clearness of thought here to consider the mechanism of an electrolytic cell. It consists of two platinum plates, one kept "positive" and the other "negative," dipping in an electrolyte, say, a solution of salt. The positive plate may be considered as analogous to a suction-pump, capable of withdrawing electrons from the solution; the negative plate, a species of electrical force-pump, giving electrons to the solution. The sodium ions move towards the source of electric pressure; each combines with an electron, and metallic sodium, or its equivalent of hydrogen, is liberated. The chlorine ions, ions because each atom of chlorine has separated from the sodium taking with it the electron of the latter, yield up each an electron to the positive plate, and the element chlorine or its equivalent in oxygen is liberated.

The action of a battery is easily pictured on the same general lines. Suppose a simple battery of a copper and a zinc plate dipping in a solution of hydrochloric acid. Electrons can pass through metallic conductors; let us accept that statement for the moment without inquiring into the mechanism. Metals are, however, impervious to ions; they form a species of semipermeable membrane. Both copper and zinc tend to throw off electrons (see Ramsay and Spencer, *Phil. Mag.*, 1906, [vi], **12**, 399), but zinc more readily than copper. So long as the metals are not externally joined, no continuous action takes place; but on making connexion, the result is this: electrons leave the zinc more rapidly and readily than they leave the copper; this induces a flow of electrons from the zinc plate through the connecting wire to the copper; on reaching the surface of the copper, these electrons, or possibly electrons displaced by them, leave the copper plate, combining with ions of hydrogen, which then escapes in the gaseous form, whilst the zinc parts with electrons and enters into solution as zinc ions. It may be asked whence the motive power is derived which causes the current of electrons through the wire; the answer may be stated in two ways: either it is due to the difference of the force with which the copper and the zinc retain their electrons, or, in ordinary language, to the electromotive force of the copper-zinc couple; or it may be attributed to a kind of osmotic pressure, the electrons traversing what to them is a nearly open road, namely, the wire, whilst matter, that is, chlorine ions, is unable to pass. This process goes on so long as there is a difference of electric pressure, so long as any zinc is left, or so long as hydrogen ions are present to take up electrons.

Let us again consider the combination of sodium with chlorine to form common salt. If it be conceded that salt differs from its solution only in so far as the mobility of the solution permits of transfer of ions, the transfer of an electron from the sodium to the chlorine must take place at the moment of combination. Symbolised, if we write E for electron and simplify the reaction, dealing for the moment with an atom and not with a molecule of chlorine, we have

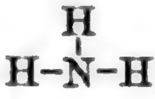
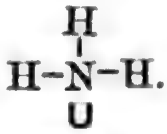
$$\mathrm{ENa} + \mathrm{Cl} = \mathrm{NaECl}.$$

Here the electron serves as the bond of union between the sodium and the chlorine.

If it be desired to form a mental picture of what occurs, let me suggest a fanciful analogy which may serve the purpose: it is that an electron is an amœba-like structure, and that ENa may be conceived as an orange of sodium surrounded by a rind of electron; that on combination, the rind separates from the orange and forms a layer or cushion between the Na and the Cl, and that on solution the electron attaches itself to the chlorine in some similar fashion, forming an ion of chlorine. It will be noticed that the E fills the place usually occupied by a bond, thus: Na–Cl. It happens providentially that the bond and the negative sign are practically the same; Na–Cl may be supposed to ionise thus: Na(–Cl), the negative charge or electron remaining with the chlorine.

Let us next consider a fundamental question, which, however, I do not remember to have seen raised. In ordinary parlance, hydrogen and chlorine are termed monads, and may be represented as each possessing a bond of affinity, thus, H–, Cl–. Now, when they unite, are there two bonds or one? Should we write H–Cl with one bond, or H––Cl with two? Considering a bond as an electron, the symbol Cl– is wrong for an atom of chlorine; it has, strictly speaking, no bond, that is, no electron, but merely possesses the power of receiving one from the hydrogen. But we know from chemical considerations, as well as from arguments derived from the ratio of the specific heats at constant volume and at constant pressure of monatomic and of diatomic gases, that the hydrogen molecule has the formula H_2, and the chlorine molecule, Cl_2. How can we explain this? Is the formula of hydrogen H–H or H––H? And is that of chlorine ClCl?

These gases conduct electricity at low pressures, and are therefore ionised. It appears probable that in this state the electric condition of the ions must be different. Several suppositions are conceivable. First, the ions may be H and EHE; second, they may be E and HEH; third, they may be E_2 and H_2. From Wilson's experiments on the separation of the ions in an electric field, and on the slower rate of motion of the positive ions, the second and third of these views are the more probable, and chemical considerations would lead, I think, to the choice of the second. When urged electrically, the electrons can penetrate thin metallic plates, as Lenard as shown. But it is a matter on which we may agree to reserve judgment.

Let us next consider the chlorine molecule. Here we have, apparently, two atoms in juxtaposition, no electron being associated with them. It must, however, be remembered that in the oxygenated compounds of chlorine, that element is a polyad, a triad in KO–Cl=0, a tetrad in O=Cl=O, a pentad in KO–Cl(=O)$_2$, and a heptad in KO–Cl(=0)$_3$. It has therefore a reserve of electrons, and when it combines with itself, forming Cl_2, we have the choice between ClECl, ClE_3Cl, ClE_5Cl, and ClE_7Cl. Were we to write out in full all the electrons, we should have the cumbrous formulæ $E_6ClEClE_7$, $E_4ClE_3ClE_7$, $E_2ClE_5E_7$, and ClE_7ClE_7, or we might draw the mediate electrons partly from both atoms of chlorine. I am far from suggesting the use of such formulæ; it is evident that in our ordinary structural or constitutional formulæ we ignore the "latent" electrons, and make use only of those which are of service for the moment. We may write for the formula of chlorine $\mathrm{Cl{-}Cl}$, or $\mathrm{Cl{\equiv}Cl}$, &c., but we gain nothing by indicating that the two atoms may be trebly bound. In fact, a structural formula shows by bonds those electrons which we deem it serviceable to represent. It may be remembered that Frankland in his "Lecture-notes" (Inorganic, p. 35) suggested that "latent atomicity" (or, as we now term it, valency) could, if desired, be represented. But he counselled to write  $\mathrm{H{-}\overset{\overset{H}{|}}{N}{-}H}$, and not  $\mathrm{H{-}\underset{\cup}{\overset{\overset{H}{|}}{N}}{-}H}$.

It will now be convenient to represent some typical formulæ in terms of electrons, remembering that we are really arguing in favour of the existence of a new element of which an atom is called an "electron."

So long as ionisable compounds are considered, this view presents no real difficulty. Let us examine a few reactions of the usual "exchange" type first, leaving the question of the disposal of electrons which are not separable by ionisation until later. As a first example, let us take the action of hydrochloric acid on silver nitrate:

$$\mathrm{H(ECl).Aq + Ag(ENO_3).Aq = AgECl + H(ENO_3).Aq.}$$

We might also write:

$$\mathrm{H|ECl.Aq + Ag|ENO_3.Aq = AgECl + H|ENO_3.Aq.}$$

$$\text{or: } \mathrm{H|{-}Cl.Aq + Ag|{-}NO_3.Aq = Ag{-}Cl + H|{-}NO_3.Aq.}$$

Here the vertical bar denotes ionisation.

Next let us write as an equation the action of an acid on sodium carbonate:

$$\mathrm{Na_2(E_2CO_3).Aq + H_2(E_2SO_4).Aq = Na_2(E_2SO_4).Aq + H_2E_2O + CE_4O_2,}$$

$$\text{or: } \mathrm{Na_2|E_2CO_3.Aq + H_2|E_2SO_4.Aq = Na_2|E_2SO_4.Aq + H_2E_2O + CE_4O_2,}$$

$$\text{or: } \mathrm{Na_2|{=}CO_3.Aq + H_2|{=}SO_4.Aq = Na_2|{=}SO_4.Aq + H_2{=}O + C{\equiv}O_2.}$$

In this instance, nothing is predicated regarding the electrons in water or in carbon dioxide, except that they serve to unite the elements. This point will be reserved.

Take next a simple case of oxidation:

$$\mathrm{2EFe(ECl)_2.Aq + Cl_2.Aq = 2Fe(ECl)_3.Aq,}$$

$$\text{or: } \mathrm{2{-}Fe|{=}Cl_2.Aq + Cl_2.Aq = 2Fe|({-}Cl)_3.Aq.}$$

Next of reduction:

$$\mathrm{2Fe(ECl)_3.Aq + E_2SnE_2Cl_2.Aq = 2EFe(ECl)_2.Aq + Sn(ECl)_4.Aq,}$$

$$\text{or: } \mathrm{2Fe|{\equiv}Cl_3.Aq + {=}Sn\underset{=}{|}\ Cl_2.Aq = 2{-}Fe|\ Cl_2.Aq + Sn|({-}Cl)_4.Aq.}$$

Such cases give little trouble. It is the formulæ of bodies which are not ionised, or only partially ionised, which require careful consideration.

It will be remembered that Professor Abegg, in a very suggestive memoir on valency (*Zeitsch. anal. Chem.*, 1904, **39**, 330), threw out the suggestion that the total valency of the elements may be taken as eight, which in each group may be taken as "normal" valencies, denoted by the + symbol, and "contra" valencies, denoted by the − symbol. The following table epitomises his suggestion:

Group	I.	II.	III.	IV.	V.	VI.	VII.
	1 +	2 +	3 +	4 +	− 3	− 2	− 1
	7 −	6 −	5 −	4 −	+ 5	+ 6	+ 7

The normal valencies are supposed by Abegg to be "stronger" than the contravalencies.

A somewhat similar hypothesis has been advanced by Arrhenius (*Theorien der Chemie*, Leipzig, 1906) and by Spiegel (*Zeitsch. anorg. Chem.*, 1894, **5**, 29, 365). To take a specific instance: nitrogen in ammonia carries as many pairs of opposite electrical units as corresponds with its maximum capacity for saturation. Thus NH_3 has an additional negative and an additional positive charge when it forms $NH_3(-H)(+Cl)$. The existence of such "neutral" affinities, according to Spiegel, explains the greater content of energy of such bodies as ammonia than their compounds like ammonium chloride.

Let us now consider the question: in compounds containing elements or groups which do not separate as ions, and which therefore do not afford a clue, from which element does the electron come? The answer is best arrived at by considering as an instance such a compound as perchloric acid. When dissolved in water, the hydrogen of $H{-}OClO_3$ is left as an ion, minus an electron, $H|{-}OClO_3$. The four atoms of oxygen are capable of receiving electrons; but the chlorine atom, having already seven attached to it, can receive only one more, and that one only when it is ionised, as in a solution of common salt. It then possesses its full complement of eight electrons. Hence it follows that in perchloric acid, the electrons which form the bonds of union of the chlorine with the oxygen must be those previously associated with the chlorine, and not those associated with the oxygen. Expressed in the cumbrous notation in which each electron is denoted by E, we should have

$$HEO(E)_4ECl\{E_2O(E)_4\}_3.$$

The $(E)_4$ means that the oxygen is normally associated with four electrons besides the two which it receives from the hydrogen and the chlorine; the second $(E)_4$ implies that each oxygen atom is associated with four electrons besides the two which it takes from the chlorine.

In Abegg's phraseology, oxygen possesses two normal valencies which are here latent, and four contravalencies (not six, for oxygen is never known to act as a hexad) which here become operative. If we read Abegg's nomenclature in the sense that a plus sign signifies the ability to part with one or more electrons, whilst a minus sign is the ability to receive one or more electrons, we find in his method of viewing the valency of the elements a close resemblance to the one I am putting forward. This instance will suffice as an indication of how the constitution of such molecules may be elucidated with some probability.

No theory would now be acceptable which did not attempt the explanation of two very remarkable phenomena; first, the extrusion of ionisable groups in such compounds as cobaltammine nitrites by further addition of ammonia, and second, the directive influence of the presence of certain substitutive elements or groups on the position into which further substituents enter. With this last is no doubt bound up the phenomenon of tautomerism, with its attendant absorption spectra. Time fails me to attempt more than to point out the lines of a possible explanation.

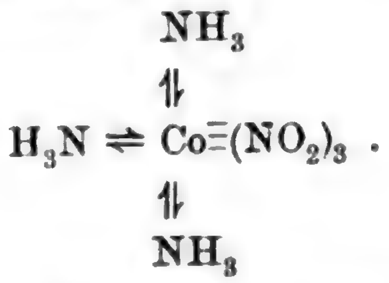
Ammonium chloride behaves like the chloride of an alkali metal, inasmuch as it yields chlorine ions when dissolved in water. We must therefore picture its partial constitutional formula as $(NH_4)|{-}Cl$, the electron, −, having become attached to the chlorine atom, converting it into an ion when dissolved in water. It is reasonable to suppose that the nitrogen atom, itself carrying five electrons, may receive three more from the three atoms of hydrogen in ammonia, thus: $H_3|{\equiv}N$. The total number of electrons now associated with the nitrogen atom is the maximum possible, eight. If an attempt be made to add another, as in NH_4, that proves impossible, but the nitrogen atom may part with one to the chlorine atom, already carrying seven, when it has a vacancy, as it were, which is filled by the electron from the hydrogen atom; it then becomes "saturated." A suggestion resembling this one has been made in terms of positive and negative charges by Arrhenius (*Theorien der Chemie*, p. 73).

Our task is now to consider the compounds investigated by Werner, and a specific case will prove sufficient. The nitrites of the cobaltammines have the peculiarity of being non-ionised, partially ionised, or completely ionised, according to the number of ammonia groups present. Thus, if the vertical bar denotes ionisation, we have:

$$Co(NO_2)_3(NH_3)_3,$$
$$Co(NO_2)_2(NH_3)_4|NO_2,\ Co(NO_2)(NH_3)_5|(NO_2)_2,\ \text{and}\ Co(NH_3)_6|(NO_2)_3.$$

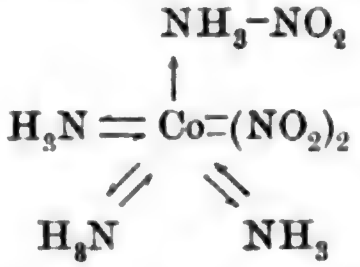
How are these compounds to be represented?

Just as the nitrogen atom in NH_4Cl takes one electron from the hydrogen of the HCl and gives one up to the chlorine, so it appears reasonable to suppose that in these cobaltammines each nitrogen atom of the three ammonia groups takes from the cobalt atom one electron, whilst it gives one at the same time. The formula of the triammino-nitrite would therefore be:



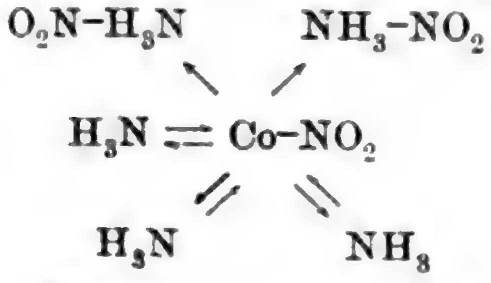
$$\begin{array}{c} NH_3 \\ \upharpoonleft\downharpoonright \\ H_3N \rightleftharpoons Co\equiv(NO_2)_3\ . \\ \upharpoonleft\downharpoonright \\ NH_3 \end{array}$$

If another molecule of ammonia be added, then the cobalt atom gives to the nitrogen of the ammonia an electron, but does not receive one in return. The nitrogen atom of that ammonia group is then "overloaded," for it has received four electrons in addition to its normal five, making nine in all; now it appears that no element can be associated with more than eight in all. Hence that nitrogen atom must lose an electron. This it imparts to one of the (NO_2)-groups, which parts company with the cobalt atom, and, as a complex ammonium nitrite is now present, it is ionisable on solution in water. A glance at the proposed formula will explain the conception:



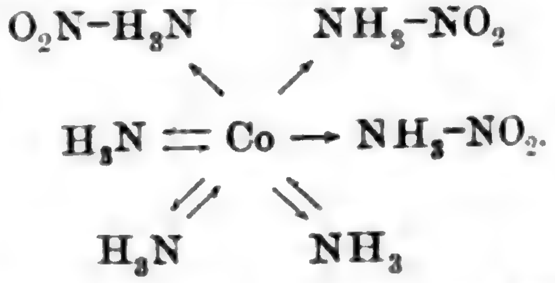
$$\begin{array}{ccc} & NH_3{-}NO_2 & \\ & \uparrow & \\ & H_3N \rightleftharpoons Co\equiv(NO_2)_2 & \\ \swarrow\!\!\nearrow & & \nwarrow\!\!\searrow \\ H_3N & & NH_3 \end{array}$$

The remaining formulæ may be written similarly, thus:



$$\begin{array}{ccc} O_2N{-}H_3N & & NH_3{-}NO_2 \\ \nwarrow & & \nearrow \\ & H_3N \rightleftharpoons Co{-}NO_2 & \\ \swarrow\!\!\nearrow & & \nwarrow\!\!\searrow \\ H_3N & & NH_3 \end{array}$$

and



$$\begin{array}{ccc} O_2N{-}H_3N & & NH_3{-}NO_2 \\ \nwarrow & & \nearrow \\ & H_3N \rightleftharpoons Co \rightarrow NH_3{-}NO_2. & \\ \swarrow\!\!\nearrow & & \nwarrow\!\!\searrow \\ H_3N & & NH_3 \end{array}$$

Why is the group $Co(NH_3)_3(NO_2)_3$ not ionisable? Let us first inquire: why is cobalt nitrate ionisable? (Cobalt nitrite is unknown.) Because the cobalt atom gives up an electron to each of the three NO_3-groups, remaining itself as an ion. That is, the metal cobalt has three electrons associated with it; what we call "metallic cobalt" is a "tri-electride" of cobalt. As "cobaltion," it has parted with its three electrons. But, in the last of the three compounds above, the cobalt has not got three electrons at disposal, it has already parted with them to the NH_3NO_2-groups. And we are led to conclude that in the non-ionisable compound the cobalt does not, as in its ordinary salts, part with three electrons, but that it receives them from the nitro-groups.

This last statement opens the difficult question why the presence of some one substituting element or group in a compound influences the position into which another substituting element or group shall enter. I can only suggest a possible answer in general terms. Non-metals are bodies which have a strong affinity for electrons; metals, bodies with but slight affinity. It is for this reason that "metallic conductors" fulfil their function, whilst non-metals are non-conductors. In a metallic wire, displacement easily occurs; whether conduction in a metal consists wholly in displacement or in flow, I do not know. Probably both methods of transit are operative. Now elements or groups already occupying a position in a compound vary in their affinity for electrons; some approximate to metals in their feeble affinity, others rather resemble non-metals. If they have a great affinity, it is likely that they will exert an attractive influence on substituents which are easily disposed to part with electrons, and vice versâ. I imagine that the phenomenon of "predisposing affinity" is to be explained in some such way.

Lastly, the phenomenon of tautomerism may be conceived as the shifting of an electron, and its accompanying absorption of light of certain parts of the spectrum as due to electronic oscillation. But it would prolong this address too far were I to enter into such speculations in detail.

I hope that I shall not be accused of presumption if I venture to draw a parallel between the past and the present. Until nearly the end of the eighteenth century, the phlogistic theory held its sway; what Lavoisier postulated as oxidation, was regarded as loss of phlogiston. I will ask you to suppose that certain persons, loth to abandon the theory of phlogiston, took a middle course, and held combustion to consist not only in the loss of phlogiston, but also in combination with oxygen. Their imaginary case, I venture to think, affords a parallel to the views of those who uphold the dual nature of electricity. Just as a combustible body may be supposed never to unite with oxygen without at the same time losing phlogiston, so, according to current language, a body never gains positive electricity without at the same time losing negative electricity. So long as electricity was supposed to be a state of matter, that view was plausible; now, however, that the substantiality of the electron has been demonstrated in so far as it exhibits inertia and possesses mass, it is surely time to reconsider our position, and, whatever the fate of the hypothesis which I have made the subject of this address, I cherish the hope that it may direct attention to a possible method of "explaining" phenomena.

As regards our Society, it still continues its era of prosperity. Our numbers increase, and our work increases. We welcome the advent of new contributors to our Transactions, and we deplore the loss of some old friends. Many, however, still remain among us, and I wish particularly to congratulate Sir William Crookes on his having attained his fiftieth year of membership, retaining the full vigour of youth. May he be long spared to enrich Science by his admirable researches!

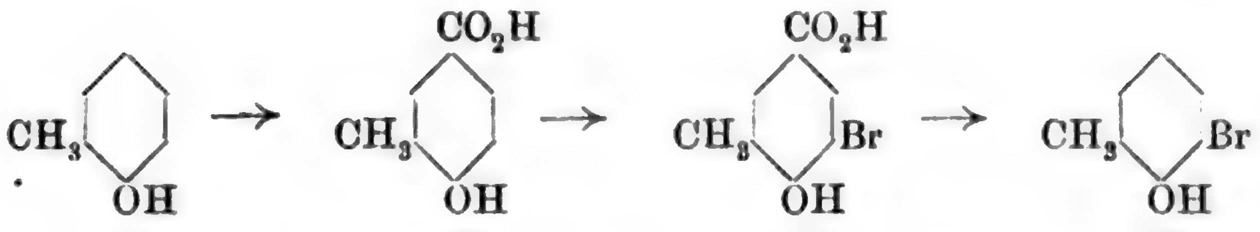
LXXI.—*Orthobromophenols and Some Bromonitrophenols.*

By Philip Wilfred Robertson.

On direct bromination with an equimolecular quantity of bromine in acetic acid solution, phenol yields both the ortho- and para-monobromo-derivatives. A method has been worked out by Meldola and Streatfeild (Trans., 1898, **73**, 681), and later extended by Hewitt, Kenner and Silk (Trans., 1904, **85**, 1225), to determine the relative amount of each isomeride produced in the reaction. The product of the bromination is nitrated and then distilled in steam; the weight of the volatile *p*-bromo-*o*-nitrophenol in the distillate gives a means of calculating the amount of *p*-bromophenol obtained from a known weight of phenol, and the amount of ortho-derivative is determined by difference.

This method was applied in the case of *o*-cresol, as it was hoped to be able to prepare a derivative containing a bromine atom in the ortho-position with respect to the hydroxyl group, namely, 3-bromo-*o*-cresol by direct bromination in acetic acid solution. It was found, however, on nitrating the product and then subjecting it to steam distillation, that practically the whole amount passed over as 5-bromo-3-nitro-*o*-cresol (m. p. 88°). Further, no trace of the isomeric 3-bromo-5-nitro-compound could be detected in the non-volatile residue, from which it must be concluded that no ortho-derivative is produced by the bromination of *o*-cresol in acetic acid solution. A second experiment, which was performed in the presence of sodium acetate, yielded a similar result.

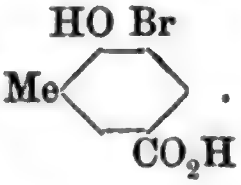
Eventually an indirect method of preparing 3-bromo-*o*-cresol (IV) was devised, which consisted in brominating 6-hydroxy-*m*-toluic acid (II) and then heating the resulting 5-bromo-6-hydroxy-*m*-toluic acid (III) with lime, as shown in the following scheme:



(I.) (II.) (III.) (IV.)

The constitution of this new bromocresol was confirmed by nitration, whereby 3-bromo-5-nitro-*o*-cresol, identical with the product of bromination of 5-nitro-*o*-cresol, was obtained.

5-*Bromo*-6-*hydroxy*-m-*toluic Acid*, Me

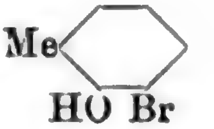


6-Hydroxy-*m*-toluic acid was dissolved in acetic acid, and the calculated quantity of a 30 per cent. solution of bromine in acetic acid was added slowly. The reaction was completed by warming on a water-bath, when the insoluble 5-*bromo*-6-*hydroxy*-m-*toluic acid* began to be deposited in fine needles. The product was recrystallised from methyl alcohol, and then melted at 227°, the yield being almost quantitative:

0·1778 gave 0·1456 AgBr. Br = 34·8.

$C_8H_7O_3Br$ requires Br = 34·6 per cent.

3-*Bromo*-o-*cresol*, Me

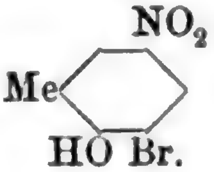


5-Bromo-6-hydroxy-*m*-toluic acid was intimately mixed, in portions of 15 grams, with about twice the amount of lime in a hard glass tube, which was heated gradually in a metal-bath to 300°. The distillation was performed in a vacuum. 3-*Bromo*-o-*cresol* collected as an oil in yields varying between 15 and 25 per cent. of the theoretical. On fractionation, practically the whole of the product boiled constantly at 199—200°/749 mm.:

0·1468 gave 0·1470 AgBr. Br = 42·5.

C_7H_7OBr requires Br = 42·7 per cent.

3-*Bromo*-5-*nitro*-o-*cresol*, Me



3-Bromo-*o*-cresol was nitrated in acetic acid solution at 0° by adding slowly a 20 per cent. solution of slightly more than the calculated quantity of nitric acid. Before the nitration was complete, white crystals had begun to separate. The product melted sharply at 120°, and the melting point remained unaltered on recrystallisation from alcohol. When obtained by the bromination of 5-nitro-*o*-cresol, the compound also melted at 120°, and on mixing the two preparations the melting point was unchanged:

0·1744 gave 0·1410 AgBr. Br = 34·4.

$C_7H_6O_3NBr$ requires Br = 34·2 per cent.

The potassium salts of this compound and of the isomeric 5-bromo-3-nitro-*o*-cresol are characterised by the fact that two varieties, one yellow and one red, can be obtained at the ordinary temperature. These substances seem to be of the same type as the "chromo-salts" of nitrophenols recently described by Hantzsch, and the results confirm the general conclusion as to the existence of two definite series of salts, red and yellow, and of orange-coloured mixed salts. As very few examples of this behaviour are well established, and, as the whole question is of considerable interest in connexion with the theoretical conclusions of Hantzsch (*Ber.*, 1907, **40**, 330), the preparation of the isomeric salts may be described.

Potassium Salts of 3-*Bromo*-5-*nitro*-o-*cresol.*

On adding a *N*/2 alcoholic solution of potassium ethoxide drop by drop to an ethereal solution of 3-bromo-5-nitro-*o*-cresol, the orange-coloured mixed salt is usually precipitated. Under certain conditions, however, the red and yellow isomerides are produced together, although generally within an hour there is a change into the orange-coloured mixed salt. If, however, excess of potassium ethoxide solution is added rapidly and with constant shaking, it is sometimes possible to precipitate the red variety alone, and when formed it appears to be moderately stable in the presence of excess of alkali. After being filtered and washed with ether, it is very unstable, and changes quickly into the orange-coloured mixed salt.

The transformation begins at one point and proceeds at a definite rate across the mass. A sample was obtained for analysis; it was free from alcohol of crystallisation by drying in a vacuum:

Found, K = 14·2.

$C_7H_5O_3NBrK$ requires K = 14·4 per cent.

The orange-coloured mixed salt, which results from the transformation of the red isomeride or on precipitation from ethereal solution, gave on analysis:

Found, K = 14·7.

$C_7H_5O_3NBrK$ requires K = 14·4 per cent.

Potassium Salts of 5-*Bromo*-3-*nitro*-o-*cresol.*

In this case, the red isomeride is the more stable and is produced when potassium ethoxide is added to the ethereal solution of the phenol. On recrystallisation from water, the colour remained unchanged. On analysis:

Found, K = 14·6.

$C_7H_5O_3NBrK$ requires K = 14·4 per cent.

The yellow variety is very unstable, but may be obtained by the cautious addition of more dilute potassium ethoxide (*N*/5) with continuous shaking. Care must be taken to avoid excess of alkali, as this causes immediate conversion. When washed with ether on the filter, the yellow isomeride generally changes rapidly into the red variety. A small quantity was obtained for analysis.

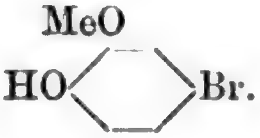
Found, K = 13·9.

$C_7H_5O_3NBrK$ requires K = 14·4 per cent.

The Monobromoguaiacols.

None of the monobromo-derivatives of guaiacol have been described. As in the case of *o*-cresol, the sole product of bromination is the para-compound, but it was found possible to obtain the ortho-derivative by the decomposition of the corresponding carboxylic acid in a manner similar to that used for the preparation of 3-bromo-*o*-cresol.

p-*Bromoguaiacol*,



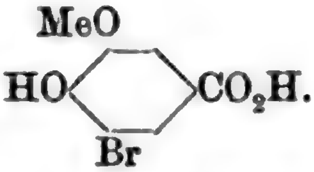
On brominating guaiacol in acetic acid in the presence of sodium acetate by the slow addition of a 30 per cent. solution of bromine at 0°, the product was obtained as an oil on pouring the solution into water. The oil was dissolved in ether, and the ethereal solution was washed several times with water and dried. After the removal of the ether, the compound was purified by distillation under diminished pressure. The *p*-bromoguaiacol distilled at 180—182°/60 mm. as an oil, which did not crystallise in a freezing mixture of ice and salt:

0·2022 gave 0·1888 AgBr. Br = 39·7.

$C_7H_7O_2Br$ requires Br = 39·4 per cent.

The constitution of this compound was proved by the fact that it yielded the same 4-bromo-6-nitroguaiacol (m. p. 120°) as that obtained by Meldola and Streatfeild (Trans., 1898, **73**, 689) by the bromination of *o*-nitroguaiacol.

2-*Bromovanillic Acid*,

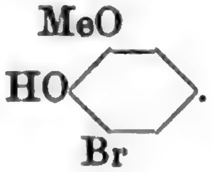


The calculated quantity of a 30 per cent. solution of bromine in acetic acid was added slowly to vanillic acid in the same solvent, in which was also contained slightly more than the theoretical amount of sodium acetate to combine with the liberated hydrogen bromide, in order to prevent the possibility of hydrolysis of the methoxyl group. During the course of the reaction, sodium bromide separated, which was dissolved by the addition of water, and then the solution was evaporated slowly to about one-third of its volume. On cooling, 2-*bromovanillic acid* separated, and was purified by recrystallisation from alcohol. It melts at 221°. The yield was 80 per cent. of the theoretical:

0·1440 gave 0·1088 AgBr. Br = 32·2.

$C_8H_7O_4Br$ requires Br = 32·4 per cent.

o-*Bromoguaiacol*,

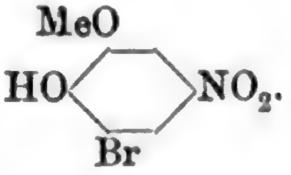


This compound was prepared by the method described in the case of 3-bromo-*o*-cresol. The product of the distillation of bromovanillic acid with lime was a solid, which after three crystallisations from methyl alcohol melted at 63°:

0·1070 gave 0·0986 AgBr. Br = 39·3.

$C_7H_7O_2Br$ requires Br = 39·4 per cent.

6-*Bromo-4-nitroguaiacol*,



The compound obtained by the nitration of *o*-bromoguaiacol, when recrystallised from alcohol, melted at 148°:

0·1092 gave 0·0822 AgBr. Br = 32·0.

$C_7H_6O_4NBr$ requires Br = 32·2 per cent.

Meldola and Streatfeild (*loc. cit.*) prepared this compound by the bromination of *p*-nitroguaiacol, and described it as melting at 142°. The differences in melting point may be possibly due to the fact that these observers crystallised their preparation from water.

Potassium Salts of the Bromonitroguaiacols.

In both cases, the red varieties tend to be the more stable.

4-*Bromo*-6-*nitroguaiacol.*—Even by the most cautious addition of dilute potassium ethoxide to the ethereal solution of the phenol, it was impossible even to obtain indications of the formation of the yellow variety. The product always appeared to be of the nature of a mixed salt, which varied in colour between a reddish-orange and an orange-red.

6-*Bromo*-4-*nitroguaiacol.*—When precipitated from the ethereal solution, the potassium salt was yellow:

Found, K = 13·7.

$C_7H_5O_4NBrK$ requires K = 13·6 per cent.

This form changed, in time, into the red isomeride:

Found, K = 13·4.

$C_7H_5O_4NBrK$ requires K = 13·6 per cent.

6-Bromo-4-nitroguaiacol is thus completely analogous to the corresponding *o*-cresol derivative.

2-*Bromothymol and Bromonitrothymol.*

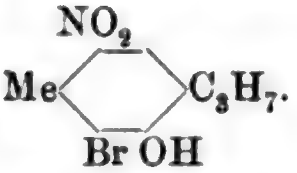
As thymotic acid is extremely difficult to obtain, it was found advisable to follow the method of Claus and Krause (*J. pr. Chem.*, 1891, [ii], **43**, 347), and to prepare 2-bromothymol by decomposing 2-bromothymol-6-sulphonic acid with hydrochloric acid in a sealed tube. In order to confirm its constitution as in the case of the orthophenols already described, it was nitrated and the same bromonitrothymol (m. p. 109°) resulted as that obtained by Kehrmann (*Annalen*, 1899, **310**, 108) by the bromination of 6-nitrothymol. However, a difficulty presents itself, as Mazzara (*Gazzetta*, 1888, **18**, 519) showed that the same compound was formed when 6-bromothymol was nitrated. In order to throw light on this apparent discrepancy, bromonitrothymol was prepared by the following methods:

(1) Nitration of 6-bromothymol (*a*) with nitric acid, (*b*) with nitrous acid; (2) bromination of 2-nitrothymol *; (3) the action of nitrous

* 2-Nitrothymol has not yet been described. A 20 per cent. solution of the calculated quantity of nitric acid in acetic acid is dropped slowly into a well-cooled solution of thymol in the same solvent. After twenty-four hours, excess of water is added, and the separated oil subjected to a steam distillation. The later fractions are crystalline and consist of pure 2-*nitrothymol*, melting at 119°, when recrystallised from water or alcohol. From the residue, 6-nitrothymol (m. p. 140°) was obtained by extraction with boiling water; this melted at the same temperature as the product obtained by Kehrmann by the oxidation of nitrosothymol.

acid on 2:6-dibromothymol (Dahmer, *Annalen*, 1904, **333**, 346); (4) bromination of 6-nitrothymol; (5) nitration of 2-bromothymol.

In all cases, however, the same bromonitrothymol was obtained, as is proved by the following considerations: (i) The melting point is always 109° and remains unaltered on mixing different preparations. (ii) The crystalline form is identical, although the habit changes slightly. (iii) The same pale yellow potassium salt is always obtained on precipitating the ethereal solution with potassium ethoxide. (iv) When reduced with tin and hydrochloric acid, oxidised with ferric chloride, and distilled with steam, the same bromothymoquinone (m. p. 48°) results in all cases.

The formation of this bromothymoquinone, and also the fact that Kehrmann (*loc. cit.*) showed that its oxime yielded the original bromonitrothymol (m. p. 109°) on mild oxidation, indicate that the compound must be 2-bromo-6-nitrothymol,  But, according to no less than three distinct methods of preparation (1, 2, 3 above), the compound should be the 6-bromo-2-nitro-derivative. From these results, it appears possible to draw only one conclusion, namely, that 6-bromo-2-nitrothymol is extremely unstable, and that immediately on its formation it is converted by a most unusual intramolecular change into the isomeric 2-bromo-6-nitrothymol.

In conclusion, the author would express his indebtedness to Mr. D. H. Nagel, Trinity College, and Mr. H. B. Hartley, Balliol College, for the kind interest they have taken in the above work.

BALLIOL AND TRINITY COLLEGE LABORATORY,
OXFORD.

LXXII.—*The Optical Activity of Compounds having Simple Molecular Structure.*

By WILLIAM JACKSON POPE and JOHN READ.

IT has been suggested that optical activity does not necessarily result from the presence of an asymmetric carbon atom in a molecular complex unless other carbon atoms are attached to the asymmetric centre (van't Hoff-Eiloart, *Arrangement of Atoms in Space*, 1898, 25); up to the present, however, very little experimental evidence bearing on the question has been put forward (Werner, *Stereochemie*, 1904, 22). The only work on the resolution of externally compensated substances of very simple molecular constitution which has been described appears to be that of Swarts on fluorochlorobromoacetic acid, $CFClBr{\cdot}CO_2H$ (*Bull. Acad. roy. Belg.*, 1896, [iii], **31**, 28); this acid contains two carbon atoms in the molecule, and on crystallisation with strychnine or cinchonine yields two isomeric salts of different specific rotatory power. After separating the alkaloid from the salts, solutions exhibiting optical activity were obtained, but the optical activity was of a fugitive character and could not be exactly measured.

The question of what degree of molecular complexity is requisite in order that the presence of an asymmetric carbon atom can give rise to optical activity, obviously possesses considerable importance in connexion with stereochemistry. For the purpose of collecting further data on the subject, we have prepared the chlorosulphoacetic acid and the chlorobromomethanesulphonic acid of Andreasch (*Monatsh.*, 1887, **7**, 159), and endeavoured to resolve them into their optically active components; both these acids contain an asymmetric carbon atom, and are of very simple molecular constitution, the former containing two and the latter but one carbon atom in the molecule. Our attempts to resolve these acids have been unsuccessful, but it seems desirable that they should be described, because, if similar negative results regularly attend such attempts, an indication will be obtained that the presence of an asymmetric carbon atom in a substance is not alone sufficient to give rise to optical activity.

Chlorosulphoacetic Acid, $CHCl(SO_3H){\cdot}CO_2H$.

The pure barium salt of chlorosulphoacetic acid, prepared as described by Andreasch, was converted into the acid by exact precipitation with sulphuric acid; the filtered solution was concentrated, and the equivalent amount of powdered strychnine dissolved in it by the aid of heat. On cooling, the normal *strychnine* salt separated in colourless, glistening needles; the mother liquors, when concentrated, deposited a further quantity of the same material, and no other salt could be obtained from the solution. The salt was crystallised several times from hot water, and showed a constant rotatory power in dilute aqueous solution; it is sparingly soluble in cold water or acetone, but dissolves readily in alcohol or hot water, and is practically insoluble in other organic solvents:

1·4079 lost 0·0312 H_2O at 110°. $H_2O = 2{\cdot}22$.

$C_{44}H_{47}O_9N_4ClS,H_2O$ requires $H_2O = 2{\cdot}09$ per cent.

0·0968, dried at 110°, gave 0·2222 CO_2 and 0·0506 H_2O. $C = 62{\cdot}60$; $H = 5{\cdot}85$.

$C_{44}H_{47}O_9N_4ClS$ requires $C = 62{\cdot}63$; $H = 5{\cdot}62$ per cent.

The crystalline salt therefore has the composition

$2C_{21}H_{22}O_2N_2,CHCl(SO_3H)\cdot CO_2H,H_2O$.

Its rotatory power was determined in aqueous solution with the following results:

0·1343 gram, made up to 20 c.c. with water, gave α_D $-0·33°$ in a 2-dcm. tube; whence $[\alpha]_D$ $-24·6°$ and $[M]_D$ $-103·6°$.

0·2025 gram, made up to 20 c.c. with water, gave α_D $-0·50°$ in a 2-dcm. tube; whence $[\alpha]_D$ $-24·7°$ and $[M]_D$ $-104·1°$.

On dissolving the salt (0·5 gram) in water, precipitating the base by addition of a slight excess of ammonia, making up the filtrate to 20 c.c. with water, and examining the solution in a 2-dcm. tube, it proved to be optically inactive. It appears therefore that the acid is contained in the normal strychnine salt in an optically inactive form, and that, if the acid is resolvable into enantiomorphously related components, the salt is a partially racemic one.

The *strychnine hydrogen* salt was prepared in the same way as the normal one, but using half the previous proportion of strychnine. The acid salt separated in light, feathery, colourless crystals, and was recrystallised from hot dilute acetone; it is much more soluble in water than the normal salt, and dissolves readily in alcohol, but is practically insoluble in other organic solvents:

0·6257 lost 0·0207 H_2O at 110°. $H_2O = 3·31$.

$C_{23}H_{25}O_7N_2ClS,H_2O$ requires $H_2O = 3·42$ per cent.

0·1065, dried at 110°, gave 0·2107 CO_2 and 0·0499 H_2O. $C = 53·96$; $H = 5·24$.

$C_{23}H_{25}O_7N_2ClS$ requires $C = 54·24$; $H = 4·95$ per cent.

The strychnine hydrogen salt thus has the composition

$C_{21}H_{22}O_2N_2,CHCl(SO_3H)\cdot CO_2H,H_2O$.

Its rotatory power was determined in aqueous solution with the following results:

0·1474 gram, made up to 20 c.c. with water, gave α_D $-0·34°$ in a 2-dcm. tube; whence $[\alpha]_D$ $-23·1°$ and $[M]_D$ $-117·4°$.

0·1630 gram, made up to 20 c.c. with water, gave α_D $-0·38°$ in a 2-dcm. tube; whence $[\alpha]_D$ $-23·3°$ and $[M]_D$ $-118·6°$.

On dissolving 0·5 gram of the salt in water and precipitating the base with ammonia as before, a solution was obtained which exhibited no optical activity in a 2-dcm. tube. It is therefore concluded that the strychnine hydrogen salt, like the normal one, contains the acid in an optically inactive form.

Salts of chlorosulphoacetic acid were also prepared with quinine, quinidine, and cinchonine; these, however, could not be obtained in a crystalline state, and consequently furnished no evidence bearing on the possibility of resolving the acid into optically active components.

Chlorobromomethanesulphonic Acid, $CHClBr\cdot SO_3H$.

This substance, containing only one carbon atom in the molecule, is apparently the simplest molecular complex containing an asymmetric carbon atom of which the resolution has been attempted. The optically inactive acid was prepared by the method given by Andreasch in the form of its barium salt, and a solution of the free acid was obtained as before by exactly precipitating the metal with sulphuric acid.

Chlorobromomethanesulphonic acid, when treated with strychnine, yields only the basic salt; on treating the hot aqueous solution of the acid with the requisite amount of strychnine, the base is readily dissolved, and, on cooling, the salt, $2C_{21}H_{22}O_2N_2,CHClBr\cdot SO_3H$, separates in small, colourless, glistening needles. After purification by several recrystallisations from hot water, the salt was analysed; it does not lose in weight by heating at 110°:

0·0954 gave 0·2038 CO_2 and 0·0474 H_2O. C = 58·26; H = 5·58.
$C_{43}H_{46}O_7N_4ClBrS$ requires C = 58·77; H = 5·28 per cent.

The following determinations of the rotatory power may be quoted:

0·1017 gram, made up to 20 c.c. with water, gave α_D − 0·25° in a 2-dcm. tube; whence $[\alpha]_D$ − 24·7° and $[M]_D$ − 107·9°.
0·1007 gram, made up to 20 c.c. with water, gave α_D − 0·25° in a 2-dcm. tube; whence $[\alpha]_D$ − 24·8° and $[M]_D$ − 108·9°.

On dissolving 0·5 gram of the salt in water, precipitating with ammonia as before, and examining in a 2-dcm. tube, the solution of ammonium chlorobromomethanesulphonate showed no appreciable optical activity. The acid was therefore not resolved into enantiomorphously related components by means of its crystalline, basic strychnine salt.

On evaporating an aqueous solution of chlorobromomethanesulphonic acid with quinidine, a resinous mass is obtained, which separates in a crystalline form after solution in hot aqueous acetone; the salt deposited from the latter solution is sparingly soluble in cold water, acetone, or alcohol, but dissolves freely in the hot solvents. After several crystallisations from hot water, the *quinidine* salt,

$$C_{20}H_{24}O_2N_2,CHClBr\cdot SO_3H,$$

is obtained in long, colourless needles, which do not lose in weight at 110°:

0·0964 gave 0·1669 CO_2 and 0·0445 H_2O. C = 47·22; H = 5·17.
$C_{21}H_{26}O_5N_2ClBrS$ requires C = 47·21; H = 4·91 per cent.

The following determinations of rotatory power were made:

0·0951 gram, made up to 20 c.c. with water, gave α_D +1·41° in a 2-dcm. tube; whence $[\alpha]_D$ +148·3° and $[M]_D$ +791°.

0·1005 gram, made up to 20 c.c. with water, gave α_D +1·47° in a 2-dcm. tube; whence $[\alpha]_D$ +146·3° and $[M]_D$ +781°.

On separating the base as before from 0·5 gram of the salt, making the solution up to 20 c.c., and examining in a 2-dcm. tube, no appreciable optical activity was observed. The acid is thus apparently not resolvable by the aid of the crystalline quinidine salt. The quinine and cinchonine salts of chlorobromomethanesulphonic acid were also prepared, but could not be obtained in the crystalline state.

If it should ultimately prove that chlorobromosulphoacetic acid and chlorobromomethanesulphonic acid can be obtained in enantiomorphously related isomerides exhibiting optical activity, it will still be remarkable that they can yield so large a number of salts with optically active bases, as are described above, whilst still retaining their optically inactive or externally compensated form. The further investigation of the subject is in progress.

MUNICIPAL SCHOOL OF TECHNOLOGY,
VICTORIA UNIVERSITY OF MANCHESTER.

LXXIII.—*The Action of Potassium Sulphite on Potassium Tetrathionate in Aqueous Solution.*

By ARTHUR COLEFAX, M.A., Barrister-at-Law.

I HAVE previously shown (Trans., 1892, **61**, 181, 1083) that iodine does not act on a mixture of a sulphite and thiosulphate in aqueous solution to form a trithionate directly, but oxidises the sulphite to sulphate and converts the thiosulphate into tetrathionate. When, however, the iodine is insufficient in quantity to oxidise all the sulphite to sulphate and convert all the thiosulphate into tetrathionate, Spring (*Bull. Acad. roy. Belg.*, 1874, [ii], **38**, 112) has shown that, in the case of the potassium salts, potassium trithionate is formed. The formation of a trithionate in such circumstances may be due to some of the unoxidised sulphite abstracting sulphur from the tetrathionate in accordance with the equation:

$$K_2SO_3 + K_2S_4O_6 = K_2S_2O_3 + K_2S_3O_6.$$

I have endeavoured in the present investigation to ascertain how far this equation represents the truth.

In previous investigations in which a sulphite was either a member of the initial system or a product of the change, I made use of the joint estimation of the total iodine titration-value and of the acidity developed in the solution after such titration was complete in determining how much of the iodine titration-value was represented by the sulphite present, and I have again employed this method.

Preparation of Potassium Trithionate, Tetrathionate, and Pentathionate.

Potassium trithionate was prepared according to the method described by Plessy (*Ann. Chim. Phys.*, 1844, [iii], **11**, 182). The salt, twice crystallised from aqueous alcohol, gave on ignition a quantity of potassium sulphate which was 64·30 per cent. of the weight of the trithionate instead of the theoretical 64·44 per cent. The aqueous solution of the salt was quite neutral, gave no precipitate with barium chloride, and occasioned no darkening in an ammoniacal solution of silver nitrate.

Potassium tetrathionate was prepared according to the method described by Kessler (*Pogg. Ann.*,1848, **74**, 249). The salt, twice crystallised from aqueous alcohol, gave on ignition a quantity of potassium sulphate which was 57·66 per cent. of the weight of the tetrathionate instead of 57·61 per cent., the theoretical quantity. The aqueous solution of the salt was neutral, and gave no indication of the presence of sulphate or pentathionate.

Potassium pentathionate: in the preparation of this salt according to the method described by Debus (Trans., 1888, **53**, 278), it was found quite possible to distinguish "six-sided prisms with pyramids only at one end" (tetrathionate) from "four-sided rhombic or six-sided star-like plates" (pentathionate).

Preliminary Experiments.

At the outset it was established that, with aqueous solutions of concentrations corresponding with those employed in the course of this research, (*a*) iodine has no appreciable immediate action on potassium trithionate, tetrathionate, or pentathionate, or on any two or all three of these salts, and (*b*) potassium sulphite and thiosulphate respectively preserve their iodine titration-values when mixed with potassium trithionate, tetrathionate, or pentathionate, or with any two or all three of these salts, provided that the titration is made within a few minutes of mixing.

With the view of ascertaining whether either potassium sulphite or thiosulphate has any action on potassium trithionate in aqueous solution, four portions of 100 c.c. of boiled distilled water saturated with carbon dioxide were taken. In each of the first three of these, 0·27 gram of potassium trithionate was dissolved, and to the second and third a quantity of potassium sulphite and thiosulphate was respectively added, so that the proportion of sulphite to trithionate was $2K_2SO_3 : K_2S_3O_6$, and of thiosulphate to trithionate, $2K_2S_2O_3 : K_2S_3O_6$. The fourth portion contained the same quantity of potassium thiosulphate as the third, but no trithionate. Each flask containing these solutions was fitted with an indiarubber stopper, through which passed two glass tubes, one serving as entrance tube for a continuously passing stream of carbon dioxide, and the second, which served as exit tube, being connected with a second flask similarly fitted and containing 100 c.c. of boiled distilled water saturated with carbon dioxide to which a small quantity of filtered starch solution and a drop of the iodine titrating solution were added.

The determination after the lapse of twenty-four hours of the iodine titration-values showed that the thiosulphate and trithionate had reacted to an extent just appreciable, but that the sulphite and trithionate had not reacted at all. The experiment also established that neither the trithionate nor the thiosulphate solution had undergone any change within the twenty-four hours. After seventy-two hours, the reaction between the thiosulphate and trithionate had progressed further, and represented, after making an allowance for the almost negligible decomposition of the trithionate solution in this period of time, a conversion of about 4 per cent. of the thiosulphate present into sulphite.

An exactly similar experiment was carried out with the view of ascertaining whether, if tetrathionate and thiosulphate are present together in aqueous solution in the proportion $K_2S_4O_6 : 2K_2S_2O_3$, any formation of sulphite could be detected. Even after seventy-two hours, no alteration in the iodine titration-value of such mixed solution, and no decomposition of the control solutions of tetrathionate and thiosulphate respectively, could be detected.

In ascertaining by means of the iodine titration, in conjunction with the developed .acidity determination, the nature and extent of the change which the sulphite undergoes, it must be noticed that in no case is the iodine titration more than a record of the quantity of converted and unconverted sulphite in the solution at any particular moment; it is not a record of the total change the sulphite may have undergone. Further, before we should be justified in deducing from a knowledge of the nature and extent of the change the sulphite has undergone, the nature and extent of the change the tetrathionate has undergone, we must ascertain whether any, and, if so, what, secondary changes are possible and whether they actually occur. If potassium sulphite and tetrathionate react in aqueous solution, the changes which should be possible would seem to be: (*a*) the direct change, $K_2SO_3 + K_2S_4O_6 = K_2S_2O_3 + K_2S_3O_6$; (*b*) re-formation of the original system if the change is reversible; (*c*) reaction between unchanged tetrathionate and potassium thiosulphate, which change may also be reversible, $K_2S_4O_6 + K_2S_2O_3 = K_2S_5O_6 + K_2SO_3$.

The determination of the iodine titration-value with the view of estimating the extent of the conversion of sulphite into thiosulphate would give no indication of this secondary change of tetrathionate into pentathionate, supposing it to occur; but such secondary change is at the expense of tetrathionate, and consequently we must ascertain whether it occurs, and to what extent, before we can deduce the nature and extent of the change the tetrathionate undergoes from a knowledge of the nature and extent of the change the sulphite suffers.

With the view of ascertaining whether this formation of pentathionate actually occurs when potassium sulphite and tetrathionate react in aqueous solution, and, if so, to what extent, the reaction of potassium pentathionate with an ammoniacal solution of silver nitrate was examined in the hope that it might possibly form an approximate quantitative method of estimating pentathionates.

The ammoniacal solution of silver nitrate was prepared by dissolving 2 grams of the crystallised salt and 50 c.c. of concentrated aqueous ammonia solution in 200 c.c. of water. The strongest solution of potassium pentathionate contained 0·361 gram dissolved in 100 c.c. Into a number of test-tubes of approximately the same diameter, portions of 10 c.c. each of the ammoniacal silver nitrate solution and an equal volume of the solution of pentathionate were run. The times were recorded which elapsed before coloration was first detectable, and, in the case of stronger solutions of pentathionate, the times were also recorded which elapsed before the coloration equalled that of an unchangeable standard. In this manner, the effect of (*a*) diminishing the concentration of the pentathionate solution, and (*b*) the presence of other substances in solution, was investigated.

(*a*) The effect of diminishing the concentration of the pentathionate solution is shown from the tabular statement on p. 802 of the results obtained.

(*b*) The effect of the presence of other substances in solution was investigated with the following results.

Using a solution of pentathionate twenty times as dilute as the strongest used in determining the effect of dilution, potassium thiosulphate, trithionate, or tetrathionate, when present in equimolecular quantities relatively to the pentathionate, did not diminish the rapidity with which the darkening with ammoniacal silver nitrate occurred in their absence. Potassium sulphite, on the other hand, not only diminished the rapidity, but also the extent of coloration. Using the twenty times diluted pentathionate solution, potassium sulphite

	First coloration detected.	Coloration equalled standard.
The strongest solution of pentathionate (0·361 gram in 100 c.c.)	Immediately.	After 10 minutes.
The strongest solution diluted 10 times	,,	,, 25 ,,
,, ,, ,, 20 ,,	Within half a minute	Coloration never equalled that of standard.
,, ,, ,, 100 ,,	Within five minutes	
,, ,, ,, 1000 ,,	Not within first hour (After 24 hours, trace of darkening detected)	

when present in quantities twice the equivalent, the equivalent, and 1/5th the equivalent proportion of the pentathionate present, retarded the first appearance of colour thirty minutes, twenty minutes, and a fraction of a minute respectively. Even after twenty-four hours the coloration in the two first cases was still extremely faint, and in the third case was unquestionably less intense than in the experiment where no sulphite had been present. It was further found that the addition of potassium sulphite to a solution of ammoniacal silver nitrate and pentathionate, in which the darkening was proceeding, arrested the same. With the exception of the latter experiment, in every case the method of performing the test was to run into the test-tubes the ammoniacal silver nitrate solution, then the solution of the substance the effect of which was to be determined, and, lastly, the pentathionate solution.

The experimental investigation of the reaction of potassium thiosulphate with potassium trithionate and tetrathionate was repeated, and the ammoniacal silver nitrate test applied to the product of such reaction. The flasks previously used were again employed, and contained (1) a solution of potassium tetrathionate and thiosulphate; (2) a solution of potassium trithionate and thiosulphate; (3) a solution of potassium tetrathionate and thiosulphate, and (4) a solution of potassium trithionate and thiosulphate. The quantity of the thiosulphate was twice the equimolecular proportion of the trithionate or tetrathionate present. The solutions contained in (1) and (2) were made with boiled water saturated with carbon dioxide, and those in (3) and (4) with ordinary distilled water. Through (1) and (2) a stream of carbon dioxide passed continuously, and through (3) and (4) a current of air was drawn for the first and last two of the twenty-four hours.

The determination of the iodine titration-value at the end of twenty-four hours of portions of 10 c.c. of the contents of the four flasks showed:

(*a*) In (1) and (3) the thiosulphate remained unchanged.

(*b*) In (2) some 3 per cent. of the thiosulphate had become converted into sulphite, and the sulphite remained as such in the solution.

(*c*) In (4) some of the thiosulphate had become converted into sulphite, and the sulphite had been partly oxidised.

The application of the ammoniacal silver nitrate test to portions of 10 c.c. of the contents of the four flasks showed: (*a*) in (1) and (3) an immediate and considerable pentathionate indication, (*b*) in (2) and (4) an extremely faint indication of pentathionate.

Hence, from these results, potassium tetrathionate and thiosulphate do react in aqueous solution to form pentathionate and sulphite, but the latter substance immediately reacts with excess of tetrathionate to form trithionate and regenerate thiosulphate. Whether the whole of the tetrathionate thus becomes converted into pentathionate and trithionate, or whether the change between thiosulphate and tetrathionate is a reversible one, the above experiment does not provide one with the means of deciding. Certainly the ammoniacal silver nitrate test points to a considerable transformation into pentathionate.

The rapid diminution in the iodine titration-value of a mixed solution of potassium sulphite and pentathionate shows that these two salts quickly react in aqueous solution. When potassium sulphite reacts in equivalent proportions with pentathionate in aqueous solution, the solution containing 0·361 gram of the pentathionate in 100 c.c., the diminution in the iodine titration-value of the solution at the end of fifteen, thirty, forty-five, and sixty minutes after mixing equalled 43·4, 46·3, 47·1, and 47·3 per cent. respectively of the initial iodine titration-value.

If the sulphite abstracts sulphur from the pentathionate and thereby becomes converted into thiosulphate, the diminution in the iodine titration-value if the reaction completed itself would equal 50 per cent. The above values clearly point to the attainment of a limit somewhere in the neighbourhood of a 50 per cent. diminution, and from them it may be inferred that the general nature of the reaction between potassium pentathionate and sulphite is that the sulphite abstracts sulphur from the pentathionate and itself becomes converted into thiosulphate. Debus has suggested that the sulphite when reacting with the pentathionate decomposes into

$$2KOH + H_2SO_3$$

(Trans., 1888, **53**, 333), and that the change proceeds according to the equation:

$$3K_2SO_3 + 2K_2S_5O_6 + 3H_2O = 5K_2S_2O_3 + 3H_2SO_3.$$

If the reaction proceeded in accordance with this equation and completed itself, the iodine titration-value, supposing no sulphur dioxide to escape, would, instead of diminishing, be increased by 83·3 per cent. Supposing the pentathionate and sulphite to have been originally present in equimolecular proportions, and supposing the excess of pentathionate to react with sulphurous acid according to the equation:

$$2H_2SO_3 + K_2S_5O_6 = K_2S_3O_6 + 2H_2S_2O_3,$$

the increase in the iodine titration-value, if the latter reaction completed itself, would be 50 per cent. The fact that in place of an increase in the iodine titration-value we have a diminution approximating to 50 per cent. shows that the general nature of the reaction is not that indicated by the former of the equations, but is the conversion of sulphite into thiosulphate and consequent abstraction of sulphur from pentathionate.

This rapid conversion of sulphite into thiosulphate and consequent abstraction of sulphur from pentathionate affords, I think, the explanation of the influence of potassium sulphite in retarding the velocity and in diminishing the extent of the coloration when the ammoniacal silver nitrate test is employed in the presence of a sulphite. Sulphur is rapidly abstracted from the pentathionate, so that the solution becomes quickly diluted in respect of the pentathionate contained in it. Of the two other explanations which theoretically might be possible, the one, that the sulphite prevents the decomposition of the pentathionate, is shown by the above experiment to be incorrect, and the other, that the pentathionate is decomposed by the ammoniacal silver nitrate solution and the sulphite itself takes up the separated sulphur, seems improbable, for silver sulphide is an insoluble compound which would be preferentially formed.

These preliminary experiments establish the following facts: (1) Potassium sulphite and trithionate do not react in aqueous solution. (2) Potassium thiosulphate and trithionate react to an appreciable extent to form sulphite and tetrathionate and the merest trace of pentathionate. (3) Potassium thiosulphate and tetrathionate react in aqueous solution to form pentathionate, the resulting sulphite being immediately reconverted into thiosulphate. (4) Potassium sulphite rapidly abstracts sulphur from pentathionate when the two salts react in aqueous solution. (5) Solutions of potassium trithionate and tetrathionate containing a gram-molecular weight per litre are stable during twenty-four hours. Iodine has no immediate action on any or all of the salts, potassium trithionate, tetrathionate, and pentathionate. Potassium thiosulphate and sulphite when present with trithionate, tetrathionate, or pentathionate, or a mixture of any or all of them, preserve their iodine titration-value, provided the thiosulphate or sulphite has not already reacted with the aqueous solution of such salt or salts.

Interaction in Aqueous Solution of Potassium Sulphite and Tetrathionate.

The aqueous solution of the sulphite and tetrathionate was contained in a tall cylinder of the capacity of 250—300 c.c., which was closed by a well-fitting indiarubber cork, through which passed a carbon dioxide entrance tube and an exit tube provided with a stop-cock. The potassium tetrathionate was dissolved in the cylinder in 175 c.c. of oiled water previously saturated with carbon dioxide, the quantity of the salt being weighed out separately each time. The sulphite solution was contained in small glass bulbs of about 30 c.c. capacity, from which the air was displaced by a stream of carbon dioxide. The sulphite solution was prepared by introducing into a dry 250 c.c. flask, from which the air had been displaced by carbon dioxide, the weighed quantity of the salt, and adding boiled out water (previously saturated with carbon dioxide) to the mark. The flask was provided with a cork, through which passed a glass tube, one end of which was connected with an apparatus generating carbon dioxide, and the other almost touched the surface of the liquid in the flask. The stop-cock of the carbon dioxide apparatus was always open, so that when the cork was removed a stream of the gas passed through the glass tube on to the surface of the sulphite solution. The bulbs were charged with the sulphite solution by withdrawing from the flask the requisite volume, 25 c.c., and running it into the bulbs, which were immediately afterwards sealed before the blowpipe. One such bulb was introduced into the cylinder containing the tetrathionate solution, and a similar one into a similar cylinder containing 175 c.c. of boiled water (previously saturated with carbon dioxide). The cork of each was replaced, and a rapid stream of carbon dioxide again passed through the liquids in the two cylinders. The bulbs were broken against the sides of the cylinders, and the contents of the cylinders well and quickly mixed partly by the stream of carbon dioxide and partly by shaking. The exact moment of breaking the bulb in the tetrathionate solution was recorded by releasing the seconds hand of a stop-watch. At intervals, 20 c.c. of the solution were withdrawn by a pipette and run into an iodine solution contained in small flasks, and the excess of iodine titrated with a solution of thiosulphate, 2 c.c. of which equalled

1 c.c. of the iodine solution. The initial sulphite titration was determined by acertaining the iodine titration-value of 20 c.c. of the contents of the cylinder, which contained no dissolved tetrathionate, and determinations after varying intervals showed that with the above precautions this initial titration-value could be preserved for twenty-four hours, that is, the sulphite could be preserved from oxidation for so long a period at least.

In the account which follows, the strength of the iodine solution is given as a record of the concentration of the solutions in which the change was proceeding, for the sulphite initially contained in 1 c.c. of such solutions required as nearly as possible 1 c.c. of the iodine solution used in the titration, and the tetrathionate, and any other substance added to the solution, was present in equivalent proportion relatively to the sulphite or in some multiple or fraction thereof.

The Change Proceeds with the Formation of Potassium Thiosulphate in Quantities Equivalent to the Sulphite which has Entered into the Reaction.

The formation of thiosulphate was proved by estimating the iodine titration-value of a solution in which the change between tetrathionate and sulphite was proceeding, and also the acidity developed when the iodine titration was completed. Methyl-orange was used as indicator in the acidity determination, the blue colour of the starch iodide being first discharged with a drop of a thiosulphate solution.

The iodine solution contained 5·08 grams in 1000 c.c. In the first experiment, the proportions of sulphite and tetrathionate were equivalent; in the second, the proportions were $K_2SO_3 : \frac{1}{2}K_2S_4O_6$. In both cases it was found that:

$$A - S = T - A,$$

where

A = Actual iodine titration-value of the solution determined at varying intervals after mixing.

S = Iodine titration-value of sulphite then present, as calculated from the developed acidity.

T = Initial iodine titration-value of the solution.

Inasmuch as the iodine titration-value of a thiosulphate is only half that of its equimolecular proportion of sulphite, the diminution of the sulphite titration by an amount twice that of the diminution in the value of the iodine titration-value of the solution shows that thiosulphate has been formed in the solution in quantities equivalent to the sulphite which has reacted with tetrathionate.

The Conversion of Sulphite into Thiosulphate is Reversible.

At first it was attempted to prove the truth of this by determining the values of the percentage change at intervals of twenty-four, forty-eight, and seventy-two hours after mixing. However, the extent to which the conversion of sulphite into thiosulphate proceeds is a considerable proportion of the theoretically complete change, and in consequence, the velocity of change after these intervals, even supposing no limit short of complete conversion to be attainable, would be extremely small. By reason of this fact and the fact also that the solution might possibly become oxidised, the method was uncertain and was consequently abandoned.

In the absence of secondary reactions, if, with the exception of variation in the active masses of the substances entering into the reaction, the conditions under which a chemical change proceeds are constant, the velocity is directly proportional to the product of the active masses of the substances between which the change is proceeding. If no secondary reaction intervenes, the amount of transformation in a given interval of time, θ, can be calculated from the equation,

$$\frac{1}{A-x}-\frac{1}{A}=a\theta,$$

where

A represents the active masses of the substances present.
$x=$ the quantity transformed in the interval of time, θ, and
$a=$ a constant.

The comparison of the values of the percentage change of sulphite into thiosulphate after varying intervals of time from the first moment of mixing with the values for the same intervals calculated from the above equation by using for a its value as determined from the observed percentage change in the first interval of time, shows a retardation of the change in excess of that due merely to dilution.

The values for a solution of potassium sulphite and tetrathionate in equivalent proportions, the concentration of which corresponded with an iodine solution containing 5·08/2 grams in 1000 c.c., gave :

	Percentage change actually occurring.	Percentage change calculated from equation.	Differences.
¼ hour after mixing	29·5	29·5	—
½ ,, ,, ...	41·9	45·5	3·6
¾ ,, ,, ...	50·2	55·6	5·4
1 ,, ,, ...	55·7	62·6	6·9

The secondary reactions which are theoretically possible in a solution in which sulphite and tetrathionate are reacting one with another are: the reverse change between thiosulphate and trithionate, the formation of pentathionate by interaction of tetrathionate and thiosulphate, and its subsequent reconversion into tetrathionate by the action of sulphite. The preliminary experiments have shown that potassium trithionate and thiosulphate do react to form tetrathionate and sulphite, and that potassium tetrathionate and thiosulphate react to form pentathionate. They have also shown how rapidly potassium pentathionate and sulphite interact. It will be subsequently shown that pentathionate is not permanently formed in a solution in which potassium tetrathionate and sulphite react in equivalent quantities. The interaction of trithionate and thiosulphate would account for a retardation of the velocity of the direct change between tetrathionate and sulphite in excess of that occasioned merely by dilution, and, from the fact disclosed by the preliminary experiments that potassium trithionate does react with thiosulphate to form sulphite and presumably tetrathionate, may, I think, be regarded as in the main responsible for the retardation, in excess of that occasioned by dilution, in the velocity with which the direct change between tetrathionate and sulphite proceeds. In other words, the change between tetrathionate and sulphite of potassium is a reversible one. However, certain results to be mentioned later are quite inconsistent with the supposition that the change is a simple reversible one uncomplicated by any secondary reactions. As will be shown later, the addition to the system of either potassium trithionate or thiosulphate, instead of retarding, accelerates the velocity of chemical change in the first hour, although the addition of either of these substances reduces the limit values.

With the view of gaining some conception of the approximate limit value for the change between sulphite and tetrathionate, portions of 20 c.c. of a solution in which the change was proceeding were sealed up in small glass bulbs, from which the air had been displaced by carbon dioxide. The solution corresponded with an iodine solution containing 5·08/2 grams in 1000 c.c., and the sulphite and tetrathionate were present in equimolecular proportions. The values of the percentage change at the end of twenty-four hours, forty-eight hours, and eight days were determined:

24 hours from first mixing, the percentage change was 91·4
48 ,, ,, ,, ,, ,, 92·7
8 days ,, ,, ,, ,, 93·1

In each case, the titrated solution was distinctly acid. The values seemingly point to a limit value somewhat less than 95 per cent.

Pentathionate is not Permanently Formed in the Solution when Potassium Sulphite and Tetrathionate react in Equivalent Proportions in Aqueous Solution.

The preliminary experiments have already shown how rapidly sulphite abstracts sulphur from pentathionate, the sulphite itself becoming converted into thiosulphate. The pentathionate, if formed when potassium sulphite and tetrathionate react in equimolecular proportions in aqueous solution, would more probably be found in a solution in which the change had been proceeding for some time. Accordingly, having sought in vain for its presence in portions of solutions in which less than 50 per cent. of the sulphite had been converted into thiosulphate, solutions in which the change had proceeded for twenty-four and forty-eight hours respectively were examined. Portions of 10 c.c. of the solutions when tested with the ammoniacal silver nitrate solution did not in either case show any darkening within the first two hours. Eighteen hours after adding the ammoniacal silver nitrate solution a darkening had developed, the intensity of which about equalled that developed in a quarter of an hour in a solution of potassium pentathionate containing 0·0361 gram in 100 c.c. The inference to be drawn is, apparently, that, until the sulphite present in the solution had become oxidised by exposure to the air, no pentathionate was permanently formed in the solution. When potassium sulphite and tetrathionate in equivalent proportions react in aqueous solution, pentathionate is not permanently formed in the solution, provided the excess of sulphite is protected from oxidation.

The Effect of Varying the Mass of the Tetrathionate, the Mass of the Sulphite Initially Present Remaining Constant.

The sulphite present corresponded with an iodine solution containing 5·08/2 grams in 1000 c.c. The tetrathionate present was in *A*, the equivalent proportion of the sulphite, in *B*, half the equivalent proportion, and in *C*, twice the equivalent proportion. The values for the percentage change were:

	A.	*B.*	*C.*
	$K_2SO_3 : K_2S_4O_6$.	$K_2SO_3 : \frac{1}{2}K_2S_4O_6$.	$K_2SO_3 : 2K_2S_4O_6$.
¼ hour after mixing	29·9	15·8	53·0
½ hour ,, ,, ...	41·6	23·3	68·3
¾ hour ,, ,, ...	50·2	28·7	75·7
1 hour ,, ,, ...	55·8	32·7	80·7
24 hours ,, ,, ...	90·8	50·5	100·0

These values are the percentage conversion of sulphite into thiosulphate actually occurring. In the case of *B*, in order that they should express the percentage of the theoretically possible conversion, they would require to be multiplied by two. In the case of *B* and *C*, the total theoretically possible conversion of sulphite into thiosulphate has taken place; the slight excess of 50·5 over 50·0 is, of course, due to oxidation. In *C*, where, after twenty-four hours, sulphite was no longer present, it was to be expected from the preliminary experiments that pentathionate would be found. The ammoniacal silver nitrate test gave an immediate darkening with 10 c.c. of the solution (*C*); pentathionate had been formed in considerable quantities.

Effect of the Presence in the System $K_2SO_3—K_2S_4O_6$ *of* (a) *Potassium Trithionate,* (b) *Potassium Thiosulphate, in Quantities Equivalent to the Sulphite.*

The concentration of the solution in respect of the sulphite initially present corresponded with an iodine solution containing 5·08/2 grams in 1000 c.c. The tetrathionate and the trithionate or thiosulphate initially present was the equivalent proportion of this quantity of sulphite:

	$K_2SO_3 : K_2S_4O_6$.	$K_2SO_3 : K_2S_4O_6 : K_2S_2O_3$.	$K_2SO_3 : K_2S_4O_6 : K_2S_3O_6$.
At the end of ¼ hour the percentage conversion of sulphite into thiosulphate was	29·9	34·8	40·8
,, ½ ,, ,, ,,	41·6	48·8	53·7
,, ¾ ,, ,, ,,	50·2	56·2	60·2
,, 1 ,, ,, ,,	55·8	61·2	64·8
,, 48 hours ,, ,,	92·3	90·0	87·0

The increase in the values for the percentage change occurring during the first hour, when thiosulphate or trithionate is present, over the corresponding values, when sulphite and tetrathionate interact in the absence of these substances, is noticeable, and clearly shows that the nature of the reaction between potassium tetrathionate and sulphite cannot be a simple reversible change. The presence of products of the change accelerates the rate of chemical change. On the other hand, the values for the interval of forty-eight hours are in both cases smaller than the corresponding percentage (92·3) for the system $K_2SO_3 : K_2S_4O_6$, and point to the reversibility of the change between potassium sulphite and tetrathionate. The fact that thiosulphate does in certain circumstances react with tetrathionate, whereas trithionate does not react with either sulphite or tetrathionate, may account for the difference in the values of the percentage change when thiosulphate and trithionate are respectively present. Although thiosulphate and tetrathionate do not form pentathionate in the presence of sulphite, there must be a tendency to the formation of pentathionate, even if pentathionate is not actually momentarily formed, when thiosulphate and tetrathionate occur in a solution even in the presence of sulphite. This tendency to the formation of, or the momentary formation of, pentathionate may conceivably account for the smaller percentage values when thiosulphate in place of trithionate is initially present.

Conclusions.

When potassium sulphite and tetrathionate are dissolved in the same aqueous solution, chemical change proceeds with the formation of thiosulphate in equimolecular proportions to the sulphite so converted. If the sulphite and tetrathionate are originally present in equimolecular proportions, the conversion of sulphite into thiosulphate does not proceed to completion, and pentathionate is not formed in appreciable quantities.

If the relative proportions in which the sulphite and tetrathionate are dissolved are either $K_2SO_3 : \frac{1}{2} K_2S_4O_6$ or $K_2SO_3 : 2K_2S_4O_6$, the theoretically complete conversion of sulphite into thiosulphate takes place, and in the latter case, when the sulphite has been wholly converted into thiosulphate, pentathionate is found in the solution in considerable quantity.

CHRIST CHURCH,
OXFORD.

LXXIV.—*The Displacement of Halogen in* l-*Phenylchloroacetic Acid by Hydroxy- and Methoxy-groups. A Contribution to the Chemistry of the Walden Inversion.*

By ALEX. MCKENZIE and GEORGE WILLIAM CLOUGH.

IN the course of the last few years, the racemising effect of alkali, more particularly during the saponification of optically active menthyl and bornyl esters, has been repeatedly observed by one of us (Trans., 1904, **85**, 378, 1249; 1905, **87**, 1373; McKenzie and Thompson, Trans., 1905, **87**, 1004; 1907, **91**, 789; McKenzie and Müller, Trans., 1907, **91**, 1814), who has in consequence been led to consider whether those results have any bearing on the formation of optically active mandelic acid from optically active phenyl-halogen-acetic acids by the so-called "Walden inversion."

The possibility of transforming an optically active compound into its enantiomorphous isomeride without first forming the *r*- (or *dl*-) compound and then resolving the latter was realised by Walden more than ten years ago. This unexpected and remarkable change* has not yet been explained. The interest in it has, however, lately been revived in consequence of various observations made by E. Fischer and his co-workers in connexion with the synthesis of polypeptides. At the present time, it may therefore be useful to give a brief résumé of the more important results so far achieved with reference to the change in question.

From the researches of Piria (*Annalen*, 1848, **68**, 349), Pasteur (*Ann. Chim. Phys.*, 1852, [iii], **34**, 46), and Piutti (*Ber.*, 1886, **19**, 1693), it appeared that *l*-asparagine, $NH_2{\cdot}CO{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$, is converted into *l*-malic acid, $CO_2H{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2H$, by the action of nitrous acid; the behaviour of *l*-aspartic acid,

$$CO_2H{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H,$$

towards nitrous acid is similar. These results were confirmed by Walden (*Ber.*, 1895, **28**, 2766), who had previously shown (*Ber.*, 1893, **26**, 214; 1895, **28**, 1287) that *l*-malic acid (or its esters) is converted into *d*-chlorosuccinic acid, $CO_2H{\cdot}CH_2{\cdot}CHCl{\cdot}CO_2H$ (or its esters) by the action of phosphorus pentachloride. The corresponding bromo-esters, formed in a similar manner from phosphorus pentabromide and *l*-malic acid, are also dextrorotatory. That the chlorosuccinic acid, produced directly either from *l*-asparagine or *l*-aspartic acid by the action of nitrosyl chloride, is lævorotatory and not dextrorotatory (Tilden and Marshall, Trans., 1895, **67**, 494; Walden, *Ber.*, 1895, **28**, 2766; 1896, **29**, 133) was accordingly a very astonishing observation when viewed with relation to the other results just quoted. Its significance was fully appreciated by Walden when he made the following statement (*Ber.*, 1895, **28**, 2772): "Ausgehend von einem einheitlichen, optisch activen und mit nur einem asymmetrischen Kohlenstoffatom begabten Körper sind wir daher im Stande, unter Anwendung von optisch inactiven, chemisch verschieden wirkenden Agentien, bei relativ niedrigen Temperaturen zweierlei active Substitutionsproducte, d.h. die beiden optischen Antipoden zu gewinnen." From the work just referred to, it was accordingly shown that *l*-asparagine (or *l*-aspartic acid) may be converted either into *l*- or *d*-chlorosuccinic acid, thus:

$$\begin{tikzcd}
l\text{-}NH_2{\cdot}CO{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H \arrow[r, "\text{(by } HNO_2)"] \arrow[d, "\text{(by NOCl)}"] & l\text{-}CO_2H{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2H \arrow[d, "\text{(by } PCl_5)"] \\
l\text{-}CO_2H{\cdot}CH_2{\cdot}CHCl{\cdot}CO_2H & d\text{-}CO_2H{\cdot}CH_2{\cdot}CHCl{\cdot}CO_2H
\end{tikzcd}$$

A change of configuration (a "Walden inversion") by the action of nitrosyl chloride, nitrous acid, or phosphorus pentachloride must therefore have taken place.

---

* "Diese Entdeckung war seit den grundlegenden Untersuchungen Pasteurs die überraschendste Beobachtung auf dem Gebiete der optisch-aktiven Substanzen," E. Fischer, *Ber.*, 1907, **40**, 489.

With the view of deciding whether the *l*-halogen-succinic acid or its *d*-isomeride is related in configuration to ordinary *l*-malic acid, Walden (*Ber.*, 1896, **29**, 133) next studied the displacement of halogen by hydroxyl in those compounds by means of silver oxide, and established the following cycle:

$$\begin{tikzcd}
l\text{-}\mathrm{CO_2H\cdot CH_2\cdot CH(OH)\cdot CO_2H} \arrow[r, "\text{(by PCl}_5\text{)}"] & d\text{-}\mathrm{CO_2H\cdot CH_2\cdot CHCl\cdot CO_2H} \arrow[d, "\text{(by Ag}_2\text{O)}"] \\
l\text{-}\mathrm{CO_2H\cdot CH_2\cdot CHCl\cdot CO_2H} \arrow[u, "\text{(by Ag}_2\text{O)}"] & d\text{-}\mathrm{CO_2H\cdot CH_2\cdot CH(OH)\cdot CO_2H} \arrow[l, "\text{(by PCl}_5\text{)}"]
\end{tikzcd}$$

When, however, potassium hydroxide was substituted for silver oxide for the purpose of displacing the halogen by hydroxyl, the optical activity of the resulting malic acid was of the opposite sign to that of the halogen-succinic acid used (Walden, *Ber.*, 1897, **30**, 3146), thus:

$$l\text{-}\mathrm{CO_2H\cdot CH_2\cdot CH(OH)\cdot CO_2H} \underset{\text{(by KOH)}}{\overset{\text{(by PCl}_5\text{)}}{\rightleftarrows}} d\text{-}\mathrm{CO_2H\cdot CH_2\cdot CHCl\cdot CO_2H}.$$

By the successive action of phosphorus pentachloride and silver oxide, it is thus possible to convert *l*-malic acid into *d*-malic acid, or vice versa.

In the displacement of halogen, either silver oxide or potassium hydroxide acts abnormally. In order to obtain information on this point, Walden (*Ber.*, 1899, **32**, 1833) studied the displacement of halogen with a large number of bases. Some of these behaved like silver oxide, and others like potassium hydroxide. The curious result was that strong bases did not behave in one way and weaker bases in the other. The determination of the sign of the rotation of the malic acid formed in each one of Walden's experiments was of more value than the absolute numerical value found. Sometimes the action of the base was incomplete; fumaric acid was often formed; the malic acid was generally extracted from the unattacked halogen acid by means of acetone, and its slight rotation greatly intensified by means of Walden's alkaline uranyl nitrate reagent. A perusal of the various values shows that marked partial racemisation had often occurred.

Walden submits arguments in favour of regarding the conversion of *l*-malic acid into dextrorotatory halogen-succinic acid as an optically normal action, that is, an action not involving a change of configuration. It is accordingly proposed by him to designate, for example, the acid obtained from phosphorus pentachloride and *l*-malic acid as *l*-chlorosuccinic acid (*Ber.*, 1899, **32**, 1855). With regard to the displacement of halogen by hydroxyl, the action of bases which behave like potassium hydroxide is regarded as in all probability optically normal and ionic. Bases which behave like silver oxide very probably act abnormally, the change in configuration being due to the formation of intermediate silver compounds.

Since *l*-chlorosuccinic acid is obtained directly from *l*-aspartic acid by means of nitrosyl chloride, and, since *d*-chlorosuccinic acid is obtained from the same source by the action of nitrous fumes and subsequent action of phosphorus pentachloride, it follows that either nitrosyl chloride or nitrous acid must act abnormally.

The Walden inversion with reference to lactic acid was studied by Purdie and Williamson (Trans., 1896, **69**, 837), who carried out the following changes:

$$d\text{-CH}_3\cdot\text{CH(OH)}\cdot\text{CO}_2\text{H} \longrightarrow l\text{-CH}_3\cdot\text{CH(OH)}\cdot\text{CO}_2\cdot\text{C}_2\text{H}_5 \xrightarrow{\text{(by PCl}_5)} d\text{-CH}_3\cdot\text{CHCl}\cdot\text{CO}_2\cdot\text{C}_2\text{H}_5 \longrightarrow d\text{-CH}_3\cdot\text{CHCl}\cdot\text{CO}_2\text{H} \xrightarrow{\text{(by Ag}_2\text{O)}} l\text{-CH}_3\cdot\text{CH(OH)}\cdot\text{CO}_2\text{H}.$$

E. Fischer (*Ber.*, 1907, **40**, 489) shows that *d*-bromopropionic acid behaves in a similar manner either with silver oxide or silver carbonate, being converted into *l*-lactic acid; with potassium hydroxide, it forms *d*-lactic acid. The behaviour of silver oxide and of potassium hydroxide is thus exactly similar to the experience of Walden in his work on the interconversion of the malic acids.

Fischer has utilised the Walden inversion for the syntheses of various optically active polypeptides (*Ber.*, 1906, **39**, 2893). For example, *r*-leucine was resolved into its optically active components by fractional crystallisation of the brucine salts of its formyl derivative; *d*-leucine, obtained in this manner, was converted by means of nitrosyl bromide into *d*-*a*-bromo*iso*hexoic acid,

$$\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CO}_2\text{H},$$

which, by the action of phosphorus pentachloride, gave *d*-*a*-bromo*iso*hexoyl chloride. The latter compound was then coupled with *l*-leucine, when *d*-*a*-bromo*iso*hexoyl-*l*-leucine,

$$\text{C}_4\text{H}_9\cdot\text{CHBr}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH(C}_4\text{H}_9)\cdot\text{CO}_2\text{H},$$

was formed, and this, by the action of ammonia, was converted into *l*-leucyl-*l*-leucine, $\text{C}_4\text{H}_9\cdot\text{CH(NH}_2)\cdot\text{CO}\cdot\text{NH}\cdot\text{CH(C}_4\text{H}_9)\cdot\text{CO}_2\text{H}$.

Amongst the other important advances made by Fischer in his studies on the Walden inversion, the following may be mentioned.

(1) Displacement of the halogen by the amino-group and vice versa. The interconversion of the active alanines and *a*-bromopropionic acids was studied (*Ber.*, 1907, **40**, 489), and the following cycle established:

$$\begin{tikzcd}
d\text{-CH}_3\cdot\text{CH(NH}_2)\cdot\text{CO}_2\text{H} \arrow[d, "\text{(by NOBr)}"] & d\text{-CH}_3\cdot\text{CHBr}\cdot\text{CO}_2\text{H} \arrow[l, "\text{(by NH}_3)"'] \\
l\text{-CH}_3\cdot\text{CHBr}\cdot\text{CO}_2\text{H} \arrow[r, "\text{(by NH}_3)"] & l\text{-CH}_3\cdot\text{CH(NH}_2)\cdot\text{CO}_2\text{H} \arrow[u, "\text{(by NOBr)}"']
\end{tikzcd}$$

The conclusion is drawn that the action of ammonia is normal and that of the nitrosyl bromide abnormal.

Fischer and Raske (*Ber.*, 1907, **40**, 1051) have also studied the interconversion of *l*-bromosuccinic acid and *d*-aspartic acid, thus:

$$l\text{-}CO_2H\cdot CH_2\cdot CHBr\cdot CO_2H \xrightarrow{\text{(by } NH_3)} d\text{-}CO_2H\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$$

and

$$l\text{-}CO_2H\cdot CH_2\cdot CH(NH_2)\cdot CO_2H \xrightarrow{\text{(by NOBr)}} l\text{-}CO_2H\cdot CH_2\cdot CHBr\cdot CO_2H\,.$$

(2) Fischer found that the same reagent may at one time act normally and at another abnormally with compounds very closely related to one another in structure. Thus, whilst *d*-alanine yields *l*-bromopropionic acid with nitrosyl bromide, the latter reagent converts ethyl *d*-alanine into ethyl *d*-bromopropionate:

$$d\text{-}CH_3\cdot CH(NH_2)\cdot CO_2H \xrightarrow{\text{(by NOBr)}} l\text{-}CH_3\cdot CHBr\cdot CO_2H$$

$$d\text{-}CH_3\cdot CH(NH_2)\cdot CO_2Et \xrightarrow{\text{(by NOBr)}} d\text{-}CH_3\cdot CH(NH_2)\cdot CO_2Et.$$

A similar result was obtained with *l*-leucine and its ester, and also with *l*-aspartic acid and its ester (Fischer and Raske, *loc. cit.*):

$$l\text{-}CO_2H\cdot CH_2\cdot CH(NH_2)\cdot CO_2H \xrightarrow{\text{(by NOBr)}} l\text{-}CO_2H\cdot CH_2\cdot CHBr\cdot CO_2H$$

$$l\text{-}CO_2Et\cdot CH_2\cdot CH(NH_2)\cdot CO_2Et \xrightarrow{\text{(by NOBr)}} d\text{-}CO_2Et\cdot CH_2\cdot CHBr\cdot CO_2Et.$$

It is considered highly probable that in the conversion of active amino-acids into the corresponding active bromo-acids, the action of the nitrosyl bromide is abnormal, whilst the action on the esters is normal. This difference in behaviour between acid and ester is not always borne out, since Fischer and Scheibler (*Ber.*, 1908, **41**, 889) have recently found an exception in the case of *l*-valine (α-amino-*iso*valeric acid), $CHMe_2\cdot CH(NH_2)\cdot CO_2H$. The bromo-compound, obtained by the action of nitrosyl bromide on *l*-valine, gives the original *l*-valine when acted on by ammonia, a behaviour which is attributed to the action of the *iso*propyl group.

The action of silver oxide has been investigated by Fischer from the same standpoint as with nitrosyl bromide. Unfortunately, the displacement of halogen by hydroxyl by the action of water and silver oxide on active bromopropionic esters took place to a very slight extent at the ordinary temperature, whilst at higher temperatures complications arose owing to partial saponification. The problem was solved, however, by combining *l*-α-bromopropionyl chloride with glycine to form *l*-bromopropionylglycine, from which, by the action of water and silver carbonate, the bromine is displaced by hydroxyl; from the resulting compound, *l*-lactic acid is obtained on hydrolysis. The following changes are thus possible:

$$l\text{-}CH_3\cdot CHBr\cdot CO_2H \xrightarrow{\text{(by } Ag_2O\text{)}} d\text{-}CH_3\cdot CH(OH)\cdot CO_2H$$

$$l\text{-}CH_3\cdot CHBr\cdot CO\cdot NH\cdot CH_2\cdot CO_2H \xrightarrow{\text{(by } Ag_2O \text{ and hydrolysis)}} l\text{-}CH_3\cdot CH(OH)\cdot CO_2H.$$

(3) Fischer is of the opinion that in Walden's experiments the actions of nitrosyl chloride and of silver oxide are in all probability abnormal, whilst the actions of nitrous acid, potassium hydroxide, and phosphorus pentachloride are normal. The Walden inversion appears to be confined to those interactions involving (*a*) the displacement of an amino-group by means of nitrosyl halide, and (*b*) the displacement of a halogen by a hydroxy-group by means of silver oxide and other bases mentioned by Walden.

(4) The Walden inversion is dependent on the presence of a carboxyl group.

In the present paper, an account is given of the displacement of halogen in *l*-phenylchloroacetic acid by the hydroxy- and methoxy-groups respectively.

Walden describes the preparation of *d*-phenylchloroacetic acid by the action of phosphorus pentachloride on *l*-mandelic acid, but we found that this method gave unsatisfactory results, owing to the large amount of racemisation which took place. *r*-Phenylchloroacetic acid was accordingly resolved by the use of morphine, the solvent used being methyl alcohol. The resulting *l*-phenylchloroacetic acid had $[\alpha]_D^{10}$ −191·8° for $c = 3{\cdot}353$ in benzene solution. Walden's chloro-acid gave $[\alpha]_D$ +132·13° under similar conditions, and apparently was not free from the *r*-form.

A favourable circumstance attending the study of this acid from the standpoint of the Walden inversion is the ease with which the halogen is completely eliminated from it. This displacement is accompanied by racemisation, which in most cases is very considerable. Partial racemisation, however, during the Walden inversion is a frequent occurrence, to which attention is repeatedly drawn both by Walden and Fischer.

The change $l\text{-}C_6H_5\cdot CHCl\cdot CO_2H \longrightarrow C_6H_5\cdot CH(OH)\cdot CO_2H$, carried out by the action of water, gave a mandelic acid which was optically inactive. In the experiments so far conducted, complete racemisation had accordingly taken place. This was an unexpected result for a change of an apparently simple nature and one conducted under mild conditions.

A mixture of *r*- and *l*-mandelic acids was obtained by the action of water on sodium *l*-phenylchloroacetate as well as by the action of aqueous sodium hydroxide on sodium *l*-phenylchloroacetate. On the other hand, a mixture of *r*- and *d*-mandelic acids was obtained by the action of water on silver *l*-phenylchloroacetate, and also by the action of silver carbonate on *l*-phenylchloroacetic acid.

The experiments described in the present paper indicate that the following transformations can be effected :

$$\begin{tikzcd}
d\text{-}C_6H_5\cdot CH(OH)\cdot CO_2H \arrow[r, shift left, "\text{(by } PCl_5\text{)}"] & l\text{-}C_6H_5\cdot CHCl\cdot CO_2H \arrow[l, shift left, "\text{(by } Ag_2O\text{)}"] \arrow[d, "\text{(by NaOH)}"] \\
d\text{-}C_6H_5\cdot CHCl\cdot CO_2H \arrow[u, "\text{(by NaOH)}"] \arrow[r, shift right, "\text{(by } Ag_2O\text{)}"'] & l\text{-}C_6H_5\cdot CH(OH)\cdot CO_2H. \arrow[l, shift right, "\text{(by } PCl_5\text{)}"']
\end{tikzcd}$$

There is no reason for supposing that the phosphorus pentachloride acts abnormally in those cases. Walden found that sodium hydroxide behaves like potassium hydroxide. If we accept the view that, in the experiments of Walden on the interconversion of the malic acids and of Purdie and Williamson and Fischer on the interconversion of the lactic acids, the action of the potassium hydroxide is normal and the action of the silver oxide is abnormal, then, *in the interconversion of the mandelic acids, sodium hydroxide behaves abnormally and silver oxide normally.*

When *l*-phenylchloroacetic acid is acted on by methyl-alcoholic sodium hydroxide or by a solution of sodium methoxide in methyl alcohol, a mixture of *r*- and *l*-phenylmethoxyacetic acids is formed. Since one of us has already shown that *l*-phenylmethoxyacetic acid is obtained by the alkylation of *l*-mandelic acid by silver oxide and methyl iodide (Trans., 1899, **75**, 753), it is thus possible to obtain from *d*-mandelic acid either *d*-phenylmethoxyacetic acid or *l*-phenylmethoxyacetic acid according to the following scheme :

$$\begin{tikzcd}
d\text{-}C_6H_5\cdot CH(OH)\cdot CO_2H \arrow[r, "\text{(by } Ag_2O \text{ and } MeI\text{)}"] \arrow[d, "\text{(by } PCl_5\text{)}"] & d\text{-}C_6H_5\cdot CH(OMe)\cdot CO_2H \\
l\text{-}C_6H_5\cdot CHCl\cdot CO_2H \arrow[r, "\text{(by MeONa)}"] & l\text{-}C_6H_5\cdot CH(OMe)\cdot CO_2H.
\end{tikzcd}$$

It is probable that the Walden inversion takes place in the action of the sodium methoxide.

Whilst it is hoped that these experiments may throw additional light on the mechanism of the Walden inversion, it can serve no useful purpose at the present time to discuss the theory of the subject, since further experimental data are required.

EXPERIMENTAL.

Action of Phosphorus Pentachloride on l-*Mandelic Acid.*

Walden (*Ber.*, 1895, **28**, 1295) describes the preparation of *d*-phenylchloroacetic acid by the action of phosphorus pentachloride on *l*-mandelic acid. The mixture was carefully heated to 160° and then fractionated under diminished pressure, when *d*-phenylchloroacetyl chloride was obtained with $[\alpha]_D$ +158° in carbon disulphide solution. By careful decomposition of this product with cold water and recrystallisation of the resulting viscous solid from light petroleum, the resulting *d*-phenylchloroacetic acid melted at 56—58° and had $[\alpha]_D$ +132·13° for $c = 3·33$ in benzene solution.

We conducted several experiments with *l*-mandelic acid, prepared from amygdalin, in the manner indicated by Walden, and obtained a dextrorotatory phenylchloroacetic acid in every case, but the optical activity of the various products was very much less than that quoted by Walden. The action took place in two phases, the formation of mandelic chloride apparently taking place below 100°; as the temperature was raised, the further action of the pentachloride in displacing the alcoholic hydroxy-group was noticed. Since, therefore, very marked racemisation occurred under the conditions employed, we were obliged to regard the method as unsuitable for the preparation of the *d*-chloro-acid in quantity, and accordingly had recourse to the resolution of the *r*-acid by the alkaloidal method.

It may be noted in this connexion that Kipping and Hunter (Trans., 1903, **83**, 1005) have also attempted, without success, to prepare *l*-phenylchloroacetyl chloride by the interaction of phosphorus pentachloride and *d*-mandelic acid. The acid chloride obtained by them was sometimes quite inactive, and they point out that it is a very difficult, if not an impossible, task to prevent partial racemisation from taking place.

Resolution of r-*Phenylchloroacetic Acid.*

r-Phenylchloroacetic acid was prepared from phosphorus pentachloride and *r*-mandelic acid according to the method of Bischoff and Walden (*Annalen*, 1894, **279**, 122). After recrystallisation from light petroleum (b. p. 60—80°), the acid melted at 78—79°, whereas Bischoff and Walden give 78°. It contained 20·75 per cent. of chlorine, the calculated amount being 20·8.

Of the various alkaloids tried for the resolution of the *r*-acid, morphine was found to be the most suitable. Water is not a convenient solvent, since the acid is very sparingly soluble in it in the cold, and the halogen is displaced with great readiness if the aqueous solution is warmed. The best results were obtained by the use of methyl alcohol as solvent, and the following experiment may be quoted as typical.

To a solution of the *r*-acid (40 grams) in 200 c.c. of cold methyl alcohol, 71 grams of morphine were added, this being the calculated amount for the formation of the normal salt. The mixture was heated with constant shaking, and, as soon as the boiling point was reached, the morphine had all dissolved. During cooling to the laboratory temperature, crystallisation began, and, after the mixture had been maintained at 8—9° for twenty-four hours, the crystals were drained off and dried on porous earthenware; yield, 76 grams. These were dissolved in 300 c.c. of warm methyl alcohol, and the solution set aside at 8—10° for twenty-four hours. The resulting 56 grams were dissolved in 300 c.c. of warm methyl alcohol, and, after twenty-four hours at about 6°, 45 grams were obtained. This product was not yet, however, a homogeneous morphine salt, but it was found convenient at this point to decompose it and then crystallise the resulting acid mixture, instead of proceeding with the crystallisation from methyl alcohol. *N*-Hydrochloric acid (120 c.c.) was accordingly added, and the chloro-acid extracted four times with ether. (In subsequent experiments, the powdered morphine salt was shaken with aqueous sodium carbonate solution, the morphine removed, the sodium salt decomposed by mineral acid, and the chloro-acid extracted with ether.) The ethereal solution, which had been dried by sodium sulphate, yielded a lævorotatory acid (12 grams), which melted at 58—62° and had the following rotation in benzene solution:

$$l=1, c=3\cdot070, \alpha_D^{10}\ -5\cdot54^\circ, [\alpha]_D^{10}\ -180\cdot5^\circ.$$

This product, after one crystallisation from light petroleum, gave 7 grams of the pure *l*-acid. It is important that the crystallisation at this point is effected with low-boiling light petroleum. The petroleum, boiling at 60—80°, which was used for the purification of the *r*-acid is not suitable.

l-*Phenylchloroacetic acid*, $C_6H_5\cdot CHCl\cdot CO_2H$, separates from light petroleum in long, glassy needles, or, if the crystallisation is conducted slowly, in hexagonal, glassy plates. It melts at 60—61°. On analysis:

0·1502 gave 0·3102 CO_2 and 0·0562 H_2O. C = 56·3; H = 4·2.

$C_8H_7O_2Cl$ requires C = 56·3; H = 4·1 per cent.

The chlorine was estimated by adding an excess of *N*/10 silver nitrate to a weighed amount of the acid, boiling with concentrated nitric acid for thirty minutes, and then titrating with *N*/10 ammonium thiocyanate.

Found, Cl = 20·7:

$C_8H_7O_2Cl$ requires Cl = 20·8 per cent.

The method is quite trustworthy for this compound, since the complete displacement of the halogen takes place so readily.

The acid is sparingly soluble in cold water, and readily so in cold ether, ethyl alcohol, benzene or chloroform.

For the determination of its specific rotation, it was dried at the ordinary temperature under diminished pressure until of constant weight. In benzene solution:

$$l = 1,\ c = 3{\cdot}345,\ \alpha_D^{12}\ -6{\cdot}39^\circ,\ [\alpha]_D^{12}\ -191^\circ.$$

This value remained constant, within the limits of experimental error, when the acid was submitted to a further crystallisation from light petroleum.

The *l*-acid, obtained from a separate resolution of 100 grams of the *r*-acid carried out on the lines already indicated, had the rotation in benzene solution:

$$l = 1,\ c = 3{\cdot}353,\ \alpha_D^{10}\ -6{\cdot}43^\circ,\ [\alpha]_D^{10}\ -191{\cdot}8^\circ.$$

The rotation was also determined in chloroform solution:

$$l = 1,\ c = 1{\cdot}650,\ \alpha_D^{11{\cdot}2}\ -2{\cdot}63^\circ,\ [\alpha]_D^{11{\cdot}2}\ -159{\cdot}4^\circ.$$

Walden gives the value $[\alpha]_D + 107{\cdot}9^\circ$ for *d*-phenylchloroacetic acid with $c = 5{\cdot}33$ in chloroform solution (*Zeitsch. physikal. Chem.*, 1895, **17**, 705).

Action of Water on l-*Phenylchloroacetic Acid.*

l-Phenylchloroacetic acid (0·85 gram) was added to 20 c.c. of water, and the mixture maintained at 100° with occasional shaking for one hour. The solution was then extracted three times with ether, and the ethereal solution dried with sodium sulphate. The resulting acid (0·72 gram), on polarimetric examination in ethyl-alcoholic solution, was found to be optically inactive. It was free from chlorine, and had the melting point of *r*-mandelic acid. The aqueous solution from which the mandelic acid had been extracted was also inactive.

In an experiment where the displacement of the halogen by the hydroxy-group took place under different temperature conditions, the result was similar. *l*-Phenylchloroacetic acid (0·213 gram) was shaken at the ordinary temperature with nearly 25 c.c. of water for about five minutes, at the end of which time all the acid had dissolved. A little water was then added until the volume of the solution was 25 c.c. The rotation observed in a 4-dcm. jacketed tube at 10° was −5·50°, fifteen minutes having elapsed before the temperature had become constant. Since, under these conditions, very little displacement of the halogen takes place, the value $[\alpha]_D^{10}\ -161{\cdot}4^\circ$ may accordingly be taken as approximately correct for the specific rotation of the acid in aqueous solution for $c = 0{\cdot}852$. After twenty-four hours at 13°, the rotation had fallen to $\alpha_D\ -5{\cdot}08^\circ$; after forty-seven hours longer at 13° to −4·54°; after thirty hours longer at 13° to −4·27°, and after seventeen hours longer at 13° to −4·16°. After fifteen days at the laboratory temperature, the rotation had diminished to −0·54°. This solution was heated at 100° for two hours, evaporated to 11 cm., and then examined in a 1-dcm. tube, when no rotation was observed.

The latter experiment, however, was carried out with very little acid, and we hope, by working with larger amounts and varying the conditions, to obtain a slightly active mandelic acid. Whilst racemisation takes place to such a large extent, it is of particular importance to know whether the resulting product of the displacement of halogen at low temperatures may, under certain conditions, be either a mixture of *r*- and *l*-mandelic acids or *r*- and *d*-mandelic acids.

The ease with which the halogen is totally displaced in *l*-phenylchloroacetic acid in the experiments quoted is striking when compared with the behaviour of *l*-bromosuccinic acid towards water as studied by Walden (*Ber.*, 1899, **32**, 1840). Walden found that from 10 grams of the latter acid, 3 grams were recovered, whilst 3 grams of fumaric acid and 2 grams of a mixture of *r*- and *l*-malic acids were formed. It would be of interest to find out whether it is the undissociated phenylchloroacetic acid which undergoes hydrolytic decomposition, as suggested by Senter (Trans., 1907, **91**, 460), in the case of chloroacetic acid.

Action of Water on Sodium l-*Phenylchloroacetate.*

A preliminary experiment showed that the halogen is displaced very readily and completely when the aqueous solution of sodium *r*-phenylchloroacetate is heated at 100° for thirty minutes. Water (16 c.c.) was accordingly added to 0·852 gram of the *l*-acid, and 4·7 c.c. of aqueous 1·06*N* sodium hydroxide (the calculated amount) added, drop by drop, with constant shaking. The solution was heated at 100° for thirty minutes, cooled, and made up to 25 c.c.; in a 4-dcm. tube, the reading a_D $-0·55°$ was observed. It must, of course, be clearly understood that this activity is due to sodium *l*-mandelate, and not to unchanged phenylchloroacetate. The mixture of *r*- and *l*-mandelic acids, extracted as usual, was free from chlorine, melted at 112—119°, weighed 0·59 gram, and gave the following rotation in ethyl-alcoholic solution:

$$l=1,\ c=5·9,\ a_D\ -0·33°,\ [a]_D\ -5·6°.$$

When the sodium salt was heated with water in more dilute solution, the result was similar. Water (3 c.c.) and 0·106*N* aqueous sodium hydroxide (47·1 c.c.) were added to 0·852 gram of the *l*-acid; the neutral solution, after being heated at 100° for one hour, was lævorotatory, giving a_D $-0·34°$ in a 4-dcm. tube. The resulting mandelic acid mixture melted as before, and had $[a]_D$ $-5·1°$ for $c=5·67$ in ethyl-alcoholic solution.

The gradual fall in rotation caused by the action of water on sodium *l*-phenylchloroacetate was next examined. *l*-Phenylchloroacetic acid (0·426 gram) was dissolved in 23·6 c.c. of 0·106*N* aqueous sodium hydroxide, the calculated amount for the formation of the sodium salt. The solution was made up to 25 c.c., and placed in a jacketed 4-dcm. tube. After the temperature had become constant at 10·5°, thirty minutes had elapsed, and the observed rotation was then −9·64°. This gives $[\alpha]_D^{10\cdot5}$ −125·4° for $c = 1\cdot924$, a value which may be taken as approximately correct for the rotation of sodium *l*-phenylchloroacetate in water. The following figures show the gradual fall in rotation; after the first day, the temperature of the solution was not maintained constant:

Time in hours.	α_D.	*t*.
1¾	−9·56°	10·5°
2¾	9·47	10·5
3¾	9·40	10·5
5	9·34	10·5
6	9·28	10·5
7	9·21	10·5
8	9·16	10·5
22	8·32	11·0
25	8·26	10·0
26	8·23	10·0
28½	8·06	12·0
32½	7·86	10·5
46½	7·16	12·5
48½	7·11	10·5
50½	−7·01°	11·5°
52½	6·91	11·5
118½	4·00	13·0
120½	3·95	15·0
123½	3·76	17·0
147½	2·96	16·0
166½	2·49	16·0
171½	2·36	16·0
193½	1·96	16·0
215½	1·59	16·0
241½	1·36	16·0
297	0·98	16·0
308½	0·89	16·0
321½	0·83	16·0

The solution was finally heated at 100° for one and a-half hours. The mandelic acid mixture extracted from it melted at 113—119°, weighed 0·3 gram, and had $[\alpha]_D$ −6·9° for $c = 1\cdot164$ in ethyl-alcoholic solution.

Action of Aqueous Sodium Hydroxide on Sodium l-*Phenylchloroacetate.*

Water (11 c.c.) containing a drop of phenolphthalein was added to 0·85 gram of *l*-phenylchloroacetic acid, and then aqueous sodium hydroxide (1·06*N*), drop by drop, at the ordinary temperature. The pink colour was permanent after the addition of 4·7 c.c.; an additional 4·7 c.c. was then added, and the solution immersed in water at 70°; when the temperature of the water-bath had been raised to 90°, the solution became colourless. The total displacement of the halogen took place under these conditions in three minutes. The solution was made up to 25 c.c., and gave α_D −0·34° in a 4-dcm. tube. On adding two drops of the standard alkali and heating to 100° for thirty minutes, the pink colour persisted. The solution was again tested polarimetrically, and found to be lævorotatory. It was acidified by hydrochloric acid, and the mandelic acid extracted as usual. The product (0·59 gram) was free from chlorine, melted at 114—119°, and gave $[\alpha]_D$ $-4·25°$ for $c=5·89$ in ethyl-alcoholic solution.

In another experiment, the displacement of the halogen was carried out under different conditions. An aqueous solution of sodium *l*-phenylchloroacetate was prepared from 0·852 gram of *l*-acid as before. The addition of the second 4·7 c.c. of alkali was carried out during eleven and a-half hours, the alkali being added in quantities from 0·5—0·2 c.c. at a time, and the temperature being gradually raised from 0° to 100°. After having been maintained at 100° for thirty minutes, the resulting solution was decolorised by the addition of two drops of dilute hydrochloric acid, made up to 33 c.c., and examined in a 4-dcm. tube. It had α_D $-0·44°$. Excess of dilute hydrochloric acid was then added, and the mandelic acid mixture extracted; yield 0·55 gram. It melted at 112—118°, was free from chlorine, and had $[\alpha]_D$ $-6·1°$ for $c=5·52$ in ethyl-alcoholic solution.

Action of Water on Silver l-*Phenylchloroacetate.*

l-Phenylchloroacetic acid (0·85 gram) was dissolved in 50 c.c. of *N*/10 aqueous sodium hydroxide, which had previously been cooled at 0°, and 50 c.c. of *N*/10 silver nitrate solution added. The precipitate of silver salt was drained off at once, 50 c.c. of water were added to it, and the mixture shaken at the ordinary temperature for thirty minutes and then allowed to remain at the ordinary temperature for twelve hours with occasional shaking. The halogen is displaced with great ease under these conditions. The residue was drained off, washed with a little cold water, and the total filtrate extracted with ether. The resulting product was free from chlorine, melted at 105—113°, and was a mixture of *r*- and *d*-mandelic acids. A determination of its specific rotation in ethyl-alcoholic solution gave the value $[\alpha]_D$ $+24·7°$ for $c=0·982$.

The aqueous filtrate, from which the precipitate of silver salt had been withdrawn, deposited silver chloride after remaining for six days in the dark; the acid extracted from the solution was also dextrorotatory.

Action of Silver Carbonate on l-*Phenylchloroacetic Acid.*

l-Phenylchloroacetic acid (1·7 grams) was dissolved in 100 c.c. of water by shaking at the ordinary temperature for two minutes. Freshly-precipitated silver carbonate, prepared from 3·5 grams of silver nitrate, was gradually added, with constant shaking, within an interval of thirty minutes. The solution became more and more turbid as the silver carbonate was added, but there was practically no evolution of carbon dioxide. The contents of the flask were then constantly shaken for one hour, when a slight evolution of gas was noted. After three more hours at the ordinary temperature, the mixture was maintained at 30° for thirty minutes, then at 40° for thirty minutes, and, finally, at 100° for one hour with occasional shaking throughout. To the cold solution, dilute hydrochloric acid was added until no further precipitate took place, and the solid then filtered and washed with water. The filtrate (140 c.c.) was dextrorotatory, giving α_D +1·34° in a 4-dcm. tube. After fifteen hours at the ordinary temperature, the solution was extracted with ether. The mandelic acid mixture was free from chlorine, melted at 104—110°, weighed 0·75 gram, and gave the following rotation in ethyl-alcoholic solution :

$$l=4\ ;\ c=2{\cdot}914,\ \alpha_D\ +5{\cdot}62^\circ,\ [\alpha]_D\ +48{\cdot}2^\circ.$$

Conversion of l-*Phenylchloroacetic Acid into* l-*Phenylmethoxyacetic Acid.*

A preliminary experiment with 3 grams of *r*-phenylchloroacetic acid (1 mol.) showed that this acid readily undergoes complete conversion into *r*-phenylmethoxyacetic acid by boiling in methyl-alcoholic solution with sodium hydroxide (2 mols.). The resulting methoxy-acid melted at 68—70°, whereas McKenzie (Trans., 1899, **75**, 753) gives 69°.

l-Phenylchloroacetic acid (0·85 gram) was dissolved in 30 c.c. of methyl alcohol, a drop of phenolphthalein added, and then 18·8 c.c. of methyl-alcoholic sodium hydroxide (0·538*N*). After remaining at 10° for twenty-four hours, the solution was boiled for thirty minutes. A little dilute hydrochloric acid was added until the pink colour was discharged, and then 3 c.c. of dilute hydrochloric acid to dissolve the solid which had separated. The solution (55 c.c.) was lævorotatory, giving α_D −1·61° in a 4-dcm. tube. An additional 2 c.c. of the standard alkali was then added, and the solution boiled for three-quarters of an hour. The colour was not discharged. Dilute hydrochloric acid was added until the solution was neutral, the bulk of the methyl alcohol distilled off, and dilute acid added until the solid had dissolved. The acid, obtained by extraction with ether, weighed 0·74 gram ; it was a mixture of *r*- and *l*-phenylmethoxyacetic acids, melted at 63—69°, and gave the following result on polarimetric examination in ethyl-alcoholic solution :

$$l=4\ ;\ c=2{\cdot}674\ ;\ \alpha_D\ -2{\cdot}63^\circ;\ [\alpha]_D\ -24{\cdot}6^\circ.$$

l-Phenylmethoxyacetic acid, prepared by the alkylation of *l*-mandelic acid by silver oxide and methyl iodide, has $[\alpha]_D$ −151·1° for $c=2{\cdot}7062$ in ethyl-alcoholic solution (McKenzie, *loc. cit.*).

The halogen was entirely eliminated, since the above product was free from chlorine.

The displacement was next carried out by aid of a methyl-alcoholic solution of sodium methoxide. A solution of 1 gram of *l*-phenylchloroacetic acid in 25 c.c. of methyl alcohol was added to a solution of 0·3 gram of sodium in 50 c.c. of methyl alcohol. The temperature of the solution was maintained for one hour at 15°, then for one hour at 35°, then for one hour at 40°, then for one hour at 50°, then for four hours at 60°, and, finally, at the boiling point of the solution for one hour. After sixty hours at the laboratory temperature, hydrochloric acid was added, and the methyl alcohol distilled off. Water was added to dissolve the residue, and the solution extracted with ether. The resulting mixture (0·9 gram) melted at 56—58°, and again consisted of the *r*- and *l*-methoxy-acids. A determination of its specific rotation in ethyl-alcoholic solution gave the result:

$$l=4\ ;\ c=3{\cdot}5184\ ;\ \alpha_D\ -5{\cdot}46°\ ;\ [\alpha]_D\ -38{\cdot}8°.$$

The acid mixture was free from chlorine.

The action of different bases on optically active phenyl-halogen-acetic acids is at present under investigation.

BIRKBECK COLLEGE,
LONDON, E.C.

LXXV.—*The Spontaneous Crystallisation of Sodium Sulphate Solutions.*

By HAROLD HARTLEY, BERNARD MOUAT JONES and GEORGE ADRIAN HUTCHINSON.

A RECENT paper by de Coppet on supersaturated solutions (*Ann. Chim. Phys.* 1907, [viii], **10**, 457) contains an account of experiments which have extended over a period of thirty years on the spontaneous crystallisation of sodium sulphate. The general result of his work was to show that the average time which elapses before a supersaturated solution crystallises spontaneously depends mainly on the extent to which it has been cooled below the temperature at which it is saturated. He found, for example, that in the case of a solution saturated with respect to $Na_2SO_4,7H_2O$ at 17·4°, the average time required for crystallisation to begin at 5·5° was 1·7 days, and at 9·5° 27·5 days. de Coppet was thus led to conclude that the tendency to crystallisation increases regularly with fall of temperature, and that there is no sudden change in the properties of a supersaturated solution as its temperature is lowered. This view is directly opposed to the results of Miers and Miss Isaac (Trans., 1906, **89**, 413, and *Proc. Roy. Soc.*, 1907, **79**, *A*, 322) and of Hartley and Thomas

(Trans., 1906, **39**, 1016), who found that a number of supersaturated solutions crystallise spontaneously at definite temperatures if they are shaken and subjected to mechanical friction.

de Coppet worked with solutions containing 39·9, 40·7, and 43·6 grams of anhydrous sodium sulphate in 100 grams of water, and his experiments were thus limited to a small part of the solubility curve; the present investigation was undertaken with the view of studying a wider range of concentration under various conditions in the hope that further work might explain the discrepancy between the two sets of observations.

Four solid phases may separate out from a solution of sodium sulphate under different conditions, namely, crystals of ice, of $Na_2SO_4,10H_2O$, of $Na_2SO_4,7H_2O$, and of anhydrous Na_2SO_4; we have succeeded in tracing the supersolubility curve (that is, the curve giving the temperature of spontaneous crystallisation for supersaturated solutions of various strengths) for three of the four phases, but in the case of the stable hydrate $Na_2SO_4,10H_2O$ we could find no definite relation between the occurrence of crystallisation and the temperature and concentration of the solution.

The method used was the same in all experiments. Weighed amounts of $Na_2SO_4,10H_2O$ (Merck) and distilled water were sealed up in small glass tubes (the weight of solution varied from 0·6 to 10 grams), and these were then warmed to a temperature at which all the solid would dissolve and shaken until all traces of crystals has disappeared. The temperature of the tube was then slowly raised or lowered with constant shaking until crystallisation occurred. As the experiments of Miers and Miss Isaac have shown that mechanical friction has an important influence in starting crystallisation, either fragments of glass or platinum tetrahedra or garnets (the crystalline form of which is not related to that of any of the substances that might crystallise) were sealed up in tubes, and it was found that the presence of these solids during shaking certainly made the results more definite, and usually diminished the amount of supersaturation required to start crystallisation. The thermometers used in these experiments were graduated in fifths or tenths of a degree, and were standardised by means of thermometers with Reichanstalt certificates.

Crystallisation of Ice.—In this series of experiments the tubes were kept in a beaker of xylene, which was cooled by a freezing mixture of ice and salt, separated from it by an air-jacket. In this way it was possible to lower the temperature gradually, and to keep it constant for as long as was necessary, the xylene being stirred by means of a small motor. It was found that the formation of ice depended to some extent on the violence of the shaking, and the results recorded were obtained by cooling the tube slowly in the bath, quickly removing them, and giving one violent shake. The time taken was so short that the temperature of the contents of the tubes could not have altered appreciably, and the results in successive experiments agreed to about 0·1°. Miers and Miss Isaac found that in tubes containing garnets, water crystallised spontaneously at −0·4°. The highest temperature at which we observed the formation of ice crystals in pure water was −0·5°. The temperatures at which ice crystallised on cooling dilute solutions of sodium sulphate are given in table I and are plotted in Fig. 1.

TABLE I.

Grams of $Na_2SO_4,10H_2O$.	Grams of water.	Parts of anhydrous Na_2SO_4 in 100 parts of water.	Temperature of crystallisation of ice.
—	—	0·0	−0·5°
0·0911	4·0085	0·99	−0·9
0·1017	1·6702	2·59	−1·3
0·2402	2·3333	5·95	−2·3
0·5182	1·9221	10·33	−3·5
0·4657	1·4822	11·79	−3·8
0·5489	1·4195	14·03	−4·5
0·6988	1·2830	18·42	−5·0
0·5979	0·8709	21·89	−5·7
1·1338	1·5165	23·26	−5·7
0·9285	1·0949	25·39	−6·2

The supersolubility curve for ice runs nearly parallel to the freezing-point curve, meeting the supersolubility curve for $Na_2SO_4,7H_2O$ at about −6°, giving rise to a point similar to that for which Miers and Miss Isaac have proposed the name "hypertectic point" in their work on mixtures of salol and betol.

Crystallisation of $Na_2SO_4,7H_2O$.—The heptahydrate is less stable than the decahydrate, and in accordance with Ostwald's law of successive reactions it is nearly always produced in the spontaneous crystallisation of solutions which yield a hydrated salt. The temperature of spontaneous crystallisation was very definite in this case, and it was not changed by violent shaking, as in the case of ice. Continued gentle shaking in a bath with the temperature falling about one degree in twenty minutes produced a sudden shower of small crystals at a definite temperature, which never varied more than 0·2° in successive experiments. The results are given in table II, and the regularity with which crystallisation occurs is shown by the supersolubility curve for $Na_2SO_4,7H_2O$ in Fig. 1.

Fig. 1.

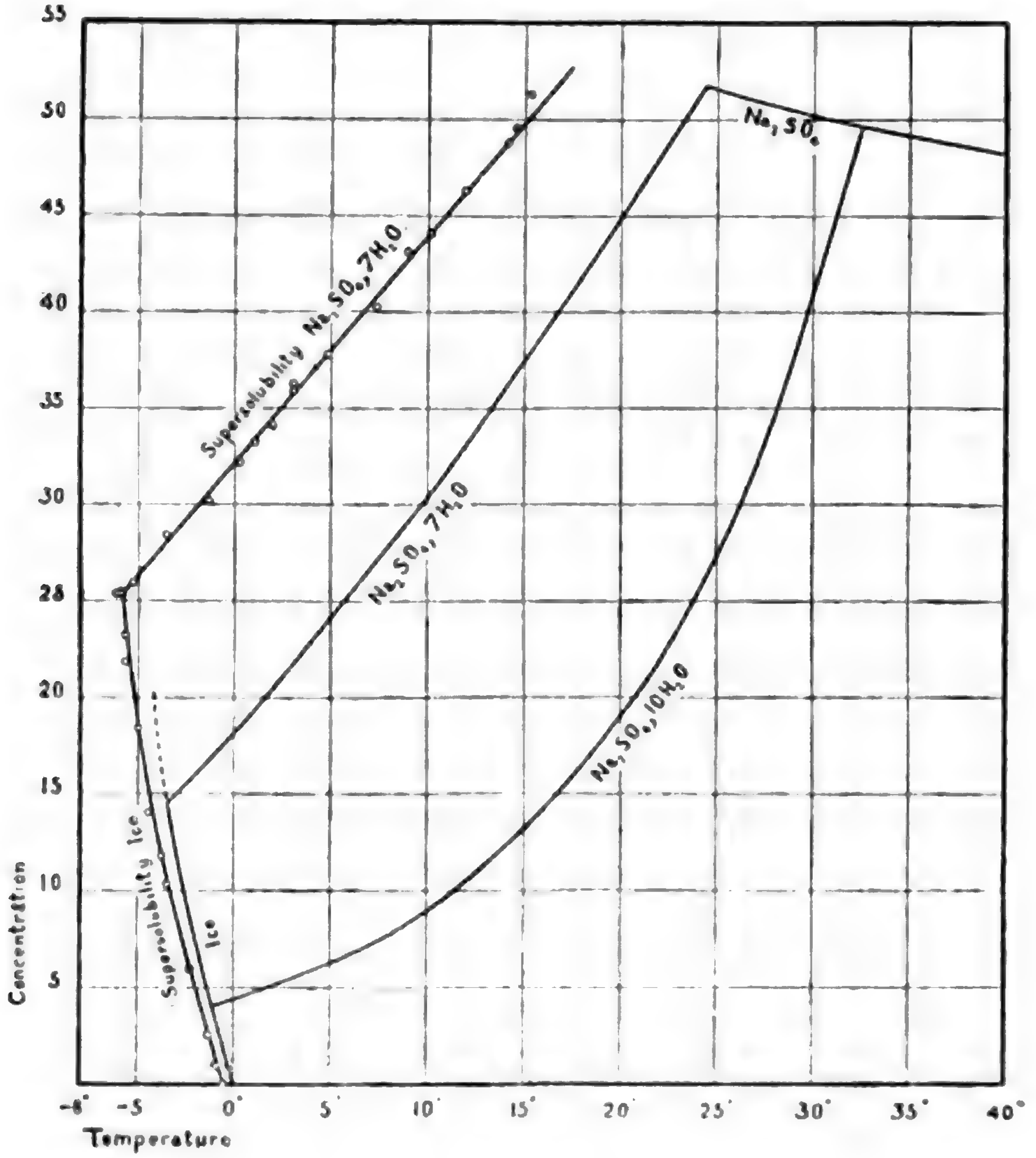


Table II.

Grams of $Na_2SO_4,10H_2O$.	Grams of water.	Parts of anhydrous Na_2SO_4 in 100 parts of water.	Temperature of crystallisation of $Na_2SO_4,7H_2O$.
0·9285	1·0949	25·39	−5·9°
0·9486	1·0799	25·99	−5·3
1·2844	1·2777	28·47	−3·6
0·9762	0·8794	30·23	−1·4
1·3844	1·1280	32·19	0·2
4·2912	3·2854	33·30	1·0
1·2429	0·9112	34·15	1·9
0·6512	0·4364	35·90	3·0
0·3903	0·2560	36·31	3·0
4·3972	2·6750	37·79	4·8
0·9034	0·5414	38·10	5·9
1·6511	0·8853	40·28	7·3
1·1397	0·5286	43·13	8·9
2·0192	0·8196	44·09	10·1
2·7508	1·0815	46·33	11·9
1·7423	0·6010	48·80	14·1
1·5570	0·5150	49·60	14·5
7·5320	2·2578	57·36	15·3

The supersolubility curve runs nearly parallel to the solubility curve, and cuts the ice curve at about −6°, a solution containing 25·4 parts of anhydrous salt per 100 of water crystallising in one experiment as $Na_2SO_4,7H_2O$ at −5·9°, and in another as ice at −6·2°.

Crystallisation of Anhydrous Sodium Sulphate.—Above 32·5°, the anhydrous salt is the most stable form of sodium sulphate, and, since its solubility decreases with rise of temperature, a saturated solution free from crystalline nuclei must be heated instead of cooled in order to produce spontaneous crystallisation. It was found that solutions of different concentrations crystallised at definite temperatures when warmed and constantly shaken; the experimental results are given in table III and plotted in Fig. 2, from which it will be seen that the supersolubility curve of the anhydrous salt gradually approaches its solubility curve as the temperature rises. The occurrence of crystallisation is not so immediately obvious in this case, owing to the abnormally slow adjustment of equilibrium in the case of crystals the solubility of which has a negative temperature-coefficient. This accounts for the fact that the supersolubility determinations do not lie on such a regular curve as in the two previous cases.

FIG. 2.

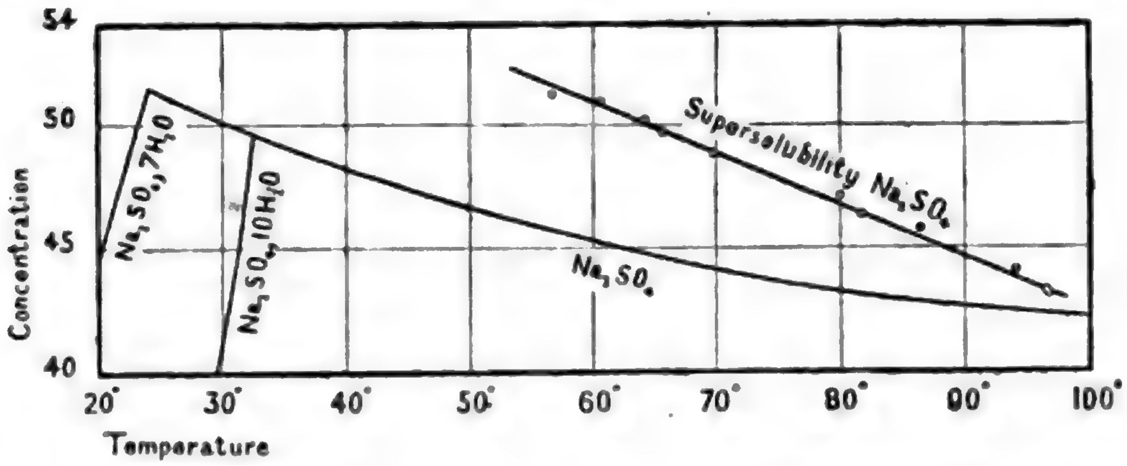


TABLE III.

Grams of $Na_2SO_4,10H_2O$.	Grams of water.	Parts of anhydrous Na_2SO_4 in 100 parts of water.	Temperature of crystallisation of Na_2SO_4.
1·1397	0·5286	43·13	97·8°
1·2278	0·5659	43·24	97·6
2·0192	0·8916	44·09	94·0
2·7221	1·1009	45·79	86·4
2·7508	1·0815	46·33	81·7
2·3059	0·8707	47·09	80·0
1·7423	0·6010	48·80	69·8
1·6311	0·5374	49·65	65·8
2·8267	0·9046	50·18	64·3
3·0410	0·9347	50·91	60·7
3·3048	0·9998	51·20	56·7

Some doubt was at first thrown on the significance of these determinations by the fact that some tubes which were not shaken continuously during heating crystallised at lower temperatures than those recorded, but this was found to be due to crystallisation taking place in the thin film of solution adhering to the glass. When the tube was not shaken, the glass was heated before the bulk of the solution, and the thin film adhering was thus caused to evaporate and its concentration was raised. This led to the crystallisation of an unstable variety of the salt (whether anhydrous or not could not be determined). The crystals were apparently orthorhombic needles, which, in contact with the solution, were observed to change into rhombic octahedra of the stable form, which acted as nuclei for further growth. This never took place in the tubes which were shaken, and this fact seems to emphasise the necessity of keeping the conditions of the solution uniform by constant agitation.

Solutions which contained no solid tended to pass over into the labile condition without crystallising, and did not give such regular results as those which were shaken with fragments of glass, garnet, or platinum. In the case of one tube, at concentration 50·95 containing no solid matter, crystallisation was observed to take place at 62·5° in one case and at 77·5° in another, whereas a similar solution containing platinum tetrahedra crystallised at 60·7°.

Crystallisation of $Na_2SO_4,10H_2O$.—When solutions containing 50 parts of Na_2SO_4 per 100 of water are cooled, the form of the solubility curves for the two hydrates $Na_2SO_4,7H_2O$ and

$$Na_2SO_4,10H_2O$$

indicates that either might crystallise. de Coppet very rarely observed the spontaneous formation of the decahydrate, and in our experiments it seldom occurred unless a solution was rapidly cooled below −10°; in about 90 per cent. of the crystallisations, $Na_2SO_4,7H_2O$ was produced. The crystallisation of the decahydrate showed no regular connexion with the temperature and concentration of the solution. Whereas with ice, $Na_2SO_4,7H_2O$, or Na_2SO_4 we could predict successfully when crystallisation would take place, the crystallisations of $Na_2SO_4,10H_2O$ seemed to be subject to no laws. For instance, a tube containing 35·9 parts of Na_2SO_4 per 100 parts of water crystallised sixteen times between 3° and −6° as the heptahydrate and once as the decahydrate, and on leaving it for some days at the room temperature it again crystallised as the decahydrate.

The existence of a definite supersolubility curve for the unstable hydrate and the lack of any definite relation in the case of the stable hydrate indicates that the dissolved salt in a strong solution is more closely related to the heptahydrate than to the decahydrate. It seems as if there are hydrated molecules in solution ready to build up nuclei of the heptahydrate, but not of the decahydrate, and the study of similar cases may throw some further light on the state of the dissolved salt in strong solutions. It is a striking fact that one hydrate should stand in such direct relation to the supersaturated solution while the other should not.

Discussion of Results.

The preceding results are based on about 800 experiments, in about half of which spontaneous crystallisation took place, so that the number of observations should be sufficient to avoid the possibility of any accidental coincidence. Except for experiments with $Na_2SO_4,10H_2O$, the results obtained lie on fairly regular curves, and they define completely the metastable and labile conditions in the system sodium sulphate-water under atmospheric pressure. Thus inspection of the solubility and supersolubility curves for the solution containing 43·13 parts per 100 parts of water shows that it is unsaturated at any temperature between 30·6° and 81·8°, if heated to 97·8° and shaken, it deposits crystals of the anhydrous salt, if cooled to 8·9° it produces the heptahydrate.

Our experiments afford additional evidence that supersaturated solutions show an abrupt change as regards their liability to crystallise when their temperature is varied, and they are inconsistent with de Coppet's conclusion that "le passage de l'état labile a l'état métastable se fait *par degrés insensible* et non pas brusquement" (*loc. cit.*, p. 592). The difference between the two results may be partly explained by the different way in which the experiments were carried out. de Coppet investigated only a small range of concentration, and his tubes were, for the most part, unshaken and did not contain any solid to produce friction. His experiments were made with the object of discovering how far time plays a part in the occurrence of crystallisation in a supersaturated solution at different temperatures, and his results are always expressed in days, the mean time taken by his solutions to crystallise being rarely less than one day. The experiments recorded here (and also those of Miers and Miss Isaac and of Hartley and Thomas) were made with the object of discovering the conditions under which a solution will invariably crystallise in the course of a few minutes. The two sets of observations do not really differ as much as might be expected, and it is not impossible to reconcile both with the theory of the metastable state.

With a solution containing 43·6 grams of Na_2SO_4 in 100 grams of water, de Coppet found that spontaneous crystallisation took place only twice in twenty tubes in thirty years at a temperature of 13·4°; below this temperature, crystallisation takes place at more frequent intervals. The curve on p. 828 shows that in our experiments crystallisation always took place at 9·5°, the solution being saturated with $Na_2SO_4,7H_2O$ at 19·3°. Again, with tubes containing 37·7 grams of salt per 100 of water, de Coppet once in thirty years observed a crystallisation at 12·1°; in our experiments, crystallisation always took place at about 6·5°.

It looks as if too rigid an interpretation had been put on the significance of the supersolubility curve, and that with long periods of time, over which the observations of de Coppet extended, crystallisation may take place within the metastable region, and in the theory put forward by Hartley and Thomas (*loc. cit.*) to account for the existence of a metastable region a possibility was omitted which may account satisfactorily for both sets of results. The existence of metastable region was supposed to be due to the increased solubility of the small crystals which are the first products of spontaneous crystallisation. The supersolubility curve was supposed to represent the solubility of these first products of crystallisation. But, as the solute molecules must possess varying amounts of kinetic energy, molecules which are in a condition to unite to form a crystal structure must often meet while a solution is still in a metastable state. It was previously assumed that under these conditions such a nucleus, being in an unsaturated solution, would dissolve again. But a molecular encounter might occasionally take place, which would suddenly produce a small crystal of such a size that its solubility would be less than the strength of the solution in which it was situated, and in this case crystallisation would occur in the metastable region. The more nearly the conditions approximated to those represented by the supersolubility curve the more frequently this would happen (as de Coppet's experiments actually show). But this possibility does not diminish the significance of the distinction between metastable and labile states, as the evidence tends to show that these chance crystallisations occur very rarely before the metastable limit is reached, at which point crystallisation always takes place under suitable physical conditions.

de Coppet disregards the increased solubility of small crystals, and tries to explain the postponement of spontaneous crystallisation in a supersaturated solution as due solely to the time which elapses before the occurrence of the particular molecular encounter which can give rise to a crystalline nucleus. If this were the only circumstance affecting crystallisation, then any supersaturated solution ought to crystallise if kept long enough, but de Coppet himself found that a considerable degree of supersaturation could be maintained for thirty years without crystallisation taking place.

Summary.

1. It has been shown that supersaturated solutions of sodium sulphate freed from crystalline nuclei crystallise at definite temperatures when subjected to mechanical friction.

2. Supersolubility curves have been traced showing the conditions under which ice, $Na_2SO_4,7H_2O$, and Na_2SO_4 are formed spontaneously from sodium sulphate solutions.

3. The spontaneous crystallisation of $Na_2SO_4,10H_2O$ is of rare occurrence as compared with that of $Na_2SO_4,7H_2O$, and it is found to bear no definite relation to the temperature and concentration of the solution.

Physical Chemistry Laboratory,
Balliol College and Trinity College,
Oxford.

Government College,
Lahore,
India.

LXXVI.—*The Existence in Aqueous Solutions of a Univalent Cadmium Ion, a Subvalent Thallium Ion, and a Bivalent Bismuth Ion.*

By Henry George Denham, M.A., M.Sc., 1851 Exhibition Scholar, University of New Zealand.

In a recent paper by Denham and Allmand (this vol., p. 424), certain anomalous results were obtained in attempting to measure the hydrolysis of lead salts by the use of the hydrogen electrode, and these could be satisfactorily explained only by the assumption that the bivalent lead ion is reduced to the univalent state in the surface film of the electrode. This conclusion was further tested by carrying out a "circulation" experiment, wherein a hot solution of lead acetate has been circulated over granulated lead for some days in order to obtain a cumulative effect; for a description of the apparatus, the original paper must be consulted. After a few days, definite metallic crystals were observed, separating out at the bottom of the column of lead. An analysis of these has since been carried out, and the percentage of lead was found to be 99·8. The low value is undoubtedly due to superficial oxidation of the crystals after their removal from the apparatus. It may be mentioned that the percentage of lead in the lowest oxide of lead (Pb_2O) is 96·3.

The separation of these crystals might conceivably be due to the formation in the hot limb of a complex anion, with a reversal of the reaction in the cold, but this view cannot be reconciled with the results obtained with the hydrogen-electrode, wherein it was proved that a reduction takes place with the consequent production of acid. The fact that both series of experiments were carried out in the absence of oxygen, excludes the possibility of such an ion as Pb^{IV} causing the phenomenon. Thus, the only explanation which appears to satisfy the results of both sets of experiments is that, under certain conditions, the bivalent lead ion may be reduced to a univalent state.

Precisely similar remarks apply to the metals, cadmium and thallium, the experiments with which will shortly be described, but in the case of bismuth the hydrogen-electrode was not used to test the reduction. However, the absence of air in the "circulation" experiment at least excludes the view that such an ion as Bi^{V} causes the separation of crystals.

A ready method for demonstrating the separation of lead crystals from solutions of lead salts lies in the use of reduced lead. If a hot solution of lead chloride be poured on a quantity of this finely-divided powder and allowed to cool, many bright crystalline faces of metallic lead may be seen scattered over the surface of the heavy powder. The effect is even better when a few pieces of granulated lead project above the bulk of the reduced metal. Crystal spikes grow from the corners of the massive metal, and, in conjunction with the experiments described previously, demonstrate the equilibria:

$$PbCl_2 + Pb \rightleftharpoons 2PbCl$$
$$Pb^{\cdot\cdot} + Pb \rightleftharpoons 2Pb^{\cdot}.$$

This experiment is extremely suitable as a lecture experiment to show the presence of a univalent lead ion.

If a hot solution of lead nitrate is used, exactly similar crystals appear, but it is advisable not to heat the solution too strongly or the presence of insoluble salts may mask the effect.

Univalent Cadmium Ion.

Nothing is known of any solid sub-salt of cadmium with the exception of the suboxide, the existence of which was first established by Tanatar and Levin (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 495) and recently confirmed by Brislee (Trans., 1908, **93**, 154).

The formation of a univalent ion of cadmium has been tested by carrying out a "circulation" experiment of the type described.

In this experiment, as well as in all succeeding ones, the column of metal in the hot limb was always broken into short sections in order to prevent any possible thermo-currents that might cause the deposition of metal. The metal was granulated, whilst the acid solution used was 4-molar-normal with respect to cadmium sulphate.

After forty hours, the lowest section of the column was found to be thickly coated on the glass with a large number of beautiful fern-like crystals. On introducing a piece of cadmium into the top of the cold condenser, crystals soon began to grow from its corners. The same peculiar case of supersaturation therefore occurs as was noticed in the case of lead. The reduction of the bivalent to the univalent ion takes place in the hot limb with absorption of heat, and one would expect the action to reverse spontaneously in the cold limb with the deposition of metallic cadmium. But this only occurs in contact with the metal, and at the ordinary temperature a solution may contain far more univalent ion than corresponds with an equilibrium condition unless crystallisation is induced by the introduction of a nucleus. Bose (*Zeitsch. Elektrochem.*, 1908, **14**, 85) has recently commented on a similar phenomenon in the $Au^{\cdot\cdot\cdot} \rightleftharpoons Au^{\cdot}$ equilibrium.

The crystalline cadmium was easily removed from the granulated metal which it enclosed, and, after washing and drying, was found to weigh 4·5 grams. This represents the yield from a five days' experiment. It is evident that if the experiment is begun with sufficiently pure materials the resulting crystalline metal must be of very great purity, for the two main factors in securing a good yield are a large metallic surface and a high ionic concentration. Thus it is extremely unlikely that any impurity would be present both in the ionic and metallic states in sufficient quantity to display any tendency to form an ion of lower electrovalency. The method therefore appears applicable for securing very pure specimens of certain metals for atomic weight determinations.

An analysis of some of the deposited crystals gave the following result: 0·6303 gram of the metal was converted into the sulphate, and weighed as such. The cadmium contained in this salt amounted to 0·6306 gram

Subvalent Thallium Ion

The apparatus contained granulated thallium, and a tenth-normal solution of thallous sulphate. After two days, small, but definite, crystals began to grow on the surface of the metal in the bottom section, and these crystals increased steadily in size. As in the previous cases of lead and cadmium, this result is best explained by assuming the reaction:

$$Tl^{\cdot} + Tl \longrightarrow Tl_2^{\cdot}.$$

$$Tl_2SO_4 + 2Tl \longrightarrow Tl_4SO_4.$$

Previously nothing has been known of any ion of thallium lower than the univalent, but this experiment shows that in all probability a subvalent ion ($Tl_2^{\cdot}$) exists in solution, and it is probable that in this we must look for an explanation of the action of light on the haloid salts of thallium. It has long been known that these salts darken under the action of light (compare Kuhlmann, *Bull. Soc. chim.*, 1864, [ii], **1**, 330; Buchner, *Sitzungsber. K. Akad. Wien*, 1865, [ii], **52**, 644, and Hebberling, *Annalen*, 1865, **134**, 11). Now Luther (*Zeitsch. physikal. Chem.*, 1899, **30**, 628) has brought forward strong evidence that the colour change of silver halides under the action of light is due to the formation of coloured sub-salts, and Bose has continued the work by demonstrating the existence of a subvalent silver ion in aqueous solution.

The existence of such a salt as Tl_4SO_4 in solution renders it probable that the action of light produces a similar effect on the thallous halides as it does on silver halides; the darkening on exposure to light would, on this assumption, be due to the formation of coloured sub-halides of thallium (Tl_2Cl, &c.).

Bivalent Bismuth Ion.

Numerous workers, among whom may be mentioned Schneider (*Pogg. Ann.*, 1855, **96**, 130), Weber (*ibid.*, 1859, **107**, 596), Heinz (*ibid.*, 1844, **63**, 55), and Berthelot (*J. Pharm.*, 1828, **14**, 616) claim to have prepared compounds of bivalent bismuth, but in no case has the resulting product been proved to be the pure substance. Some years ago Tanatar (*Zeitsch. anorg. Chem.*, 1901, **27**, 437) brought forward strong evidence in favour of the existence of bismuth suboxide, whilst Brislee (*loc. cit.*) has recently confirmed his conclusions.

In order to investigate the possibility of an ion of lower valency than $Bi^{\cdot\cdot\cdot}$, a "circulation" experiment has been carried out. The metal was, as usual, granulated, and the solution was a saturated solution of bismuth oxychloride in hydrochloric acid. After four days, tiny crystals were noticed a short distance from the bottom of the column of metal. Moreover, a piece of metal which projected at least an inch above the top of the steam jacket also showed distinct signs of adhering crystals. The temperature of the solution in the neighbourhood of these crystals was found to be 94°, that is, a drop of six degrees was sufficient to cause a marked reversal of the ionic reaction. But as this fall in temperature might give rise to a weak thermo-current with the consequent deposition of metal, the projecting piece of metal was removed, glass beads introduced, and on these a piece of bismuth placed. In twelve hours, this piece had assumed a bright crystalline appearance, due to the large number of small adhering crystals.

It is of interest that the crystals do not first appear quite at the bottom of the column, where crystallisation from the cold saturated solution might be expected. In the lead experiments, it was noticed, but not recorded, that a nucleus of metal does not induce crystallisation when the temperature is below 50°; here, as well as in the above case of bismuth, the phenomenon is probably due to the velocity of crystallisation being extremely small below that temperature.

The deposition of crystals in the above experiment is in all probability due to the reduction of the tervalent ion to one of lower electrovalency, and, in conformity with what is known concerning the sub-salts of bismuth, $BiCl_2$ and BiO, we must regard that ion as the bivalent one.

Sub-salts of Nickel, Antimony, and Arsenic.

Although a suboxide of nickel has been described, no signs of crystallisation were obtained in a "circulation" experiment with nickel and nickel sulphate solution. As it must be less difficult to obtain an aqueous solution of a sub-salt than to prepare the solid substance, this result seems to throw doubt on the existence of the suboxide.

In the case of arsenic and antimony, no sign of crystal growth had occurred when the metal was heated for ten days in contact with an acid solution of the chloride, although this is probably due to the low concentration of the metallic ion.

Summary.

1. Evidence has been brought forward for the existence of lead sub-chloride and sub-nitrate in aqueous solution.
2. The existence of cadmium sub-sulphate and of a univalent cadmium ion in aqueous solution has been rendered tolerably certain.
3. The presence of a subvalent ion of thallium has been similarly investigated, and it is probable that the darkening of thallous haloids in light is due to the formation of sub-haloids.
4. The tervalent bismuth ion has been reduced to the bivalent state in aqueous solution.
5. A negative result has been obtained for nickel, arsenic, and antimony.

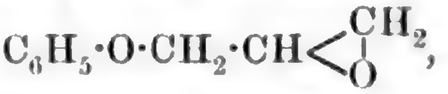
In conclusion, I wish to thank Professor F. G. Donnan for the facilities and advice which he has placed at my disposal during the course of these experiments.

MUSPRATT LABORATORY OF PHYSICAL AND ELECTRO-CHEMISTRY,
UNIVERSITY OF LIVERPOOL.

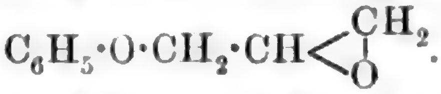
LXXVII.—*The Condensation of Epichlorohydrin with Phenols.*

By David Runciman Boyd and Ernest Robert Marle.

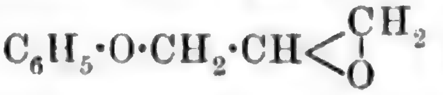
Our attention has recently been drawn to a paper on the above subject by Cohn and Plohn (*Ber.*, 1907, **40**, 2597), in which paper the authors describe some experiments on the action of epichlorohydrin on alkaline solutions of phenols, and maintain that, as the result of their experiments, certain data in the literature require correction.

The data which it is proposed to alter are those established by Lindemann (*Ber.*, 1891, **24**, 2145). This investigator found (1) that by the action of epichlorohydrin on a cold solution of phenol in aqueous sodium hydroxide an oil is obtained (b. p. 234°), to which he assigned the formula  $C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CH\Big\langle\begin{smallmatrix}CH_2\\|\\O\end{smallmatrix}$, and (2) that if epichlorohydrin is boiled for a short time with an alcoholic solution of phenol and sodium ethoxide a crystalline substance is formed (m. p. 80—81°), to which he assigned the formula $C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}O{\cdot}C_6H_5$.

Lindemann further states that the phenyl glycide ether is converted into the glyceryl diphenyl ether by boiling with an alcoholic solution of phenol and sodium ethoxide.

It is now maintained by Cohn and Plohn that the oil and the crystalline compound obtained by Lindemann are really identical; the oil, according to their statement, changing into the crystals if allowed to stand for some time. Moreover, Cohn and Plohn have analysed the crystalline compound, and obtained figures which lead them to assign to it the formula  $C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CH\Big\langle\begin{smallmatrix}CH_2\\|\\O\end{smallmatrix}$.

These conclusions of Cohn and Plohn we cannot accept.

The formula  $C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CH\Big\langle\begin{smallmatrix}CH_2\\|\\O\end{smallmatrix}$ for the crystalline compound is quite inconsistent with the results obtained by one of us (Boyd, Trans., 1901, **79**, 1221) in a study of the action of the chlorides of phosphorus on this substance. It was then shown that this compound is converted by means of phosphorus trichloride into a phosphorous acid derivative, the analysis and reactions of which pointed clearly to the formula $C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CH(OPH_2O_2){\cdot}CH_2{\cdot}O{\cdot}C_6H_5$, whilst phosphorus pentachloride transforms it into a substance for which analysis indicates the formula $C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CHCl{\cdot}CH_2{\cdot}O{\cdot}C_6H_5$.

These results confirm Lindemann's conception of the crystalline compound as a glyceryl diphenyl ether,

$$C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}O{\cdot}C_6H_5.$$

In view, however, of the statements of Cohn and Plohn, we have thought it desirable again to prepare and analyse a specimen of the crystalline substance. Our results are in complete agreement with the formula assigned by Lindemann.

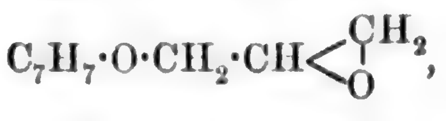
With regard to the constitution of the oil, the data in the literature are not so complete. In addition therefore to analysing this substance, we have studied its transformation into glyceryl diphenyl ether by the action of phenol in presence of alkali, and have also investigated its behaviour towards phosphorus pentachloride. Assuming Lindemann's formula $C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CH{<}\begin{array}{l}CH_2\\ |\\ O\end{array}$ to be correct, one would expect to obtain a substance of the formula $C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CHCl{\cdot}CH_2Cl$ as the principal product of the action of phosphorus pentachloride. This expectation was fully realised, the yield of phenoxydichloropropane amounting to 63 per cent. of that theoretically possible.

If the oil is allowed to stand in contact with a solution of phenol in aqueous potassium hydroxide, it reacts slowly even in the cold to form glyceryl diphenyl ether, and this change is brought about rapidly on heating an alcoholic solution of it with phenol and sodium ethoxide. From 2·18 grams of the oil, we obtained in this way 3·03 grams of the crystals, or about 85 per cent. of the theoretical yield. These results, we consider, definitely establish the formula $C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CH{<}\begin{array}{l}CH_2\\ |\\ O\end{array}$ for the oil.

We are at a loss to account for the statement of Cohn and Plohn that the oil changes into the crystalline compound on standing, except on the supposition that these investigators have never obtained the oil in a pure state. A specimen of pure phenyl glycide ether has been kept in this laboratory for a period of more than six months without undergoing any change.

It appears probable that the origin of the errors into which Cohn and Plohn have been led is to be found in the circumstance that in the preparation of phenyl glycide ether by the action of epichlorohydrin on a solution of phenol in aqueous sodium hydroxide it is scarcely possible to avoid the formation of a considerable amount of the crystalline glyceryl diphenyl ether at the same time

In the case of the action of epichlorohydrin on *p* cresol, precisely similar relations hold good. The crystalline compound (m. p. 88°), which is stated by Cohn and Plohn to have the formula



$$C_7H_7{\cdot}O{\cdot}CH_2{\cdot}CH{<}\begin{array}{l}CH_2\\ |\\ O\end{array},$$

is really, as stated by Lindemann, the glyceryl di-*p*-tolyl ether, $C_7H_7{\cdot}O{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}O{\cdot}C_7H_7$ (compare Boyd, *loc. cit.*, and

Trans., 1903, **83**, 1140), whilst the *p*-tolyl glycide ether is an oil boiling at 136° under 17 mm. pressure.

EXPERIMENTAL.

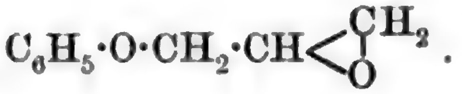
Glyceryl Diphenyl Ether, $C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}O{\cdot}C_6H_5$.

Twelve grams of sodium (rather more than 0·5 gram-atom) were dissolved in 250 c.c. of alcohol. Ninety-four grams of phenol (1 gram-mol.) were added, and then 45 grams of epichlorohydrin (rather less than 0·5 gram-mol.). The mixture was heated in a water-bath under reflux for four hours, and then poured into water. A white, crystalline solid separated. After recrystallisation from alcohol, it melted at 81—82°. The yield was 90 grams.

It is to be noted that the maximum yield of phenyl glycide ether which is theoretically possible from 45 grams of epichlorohydrin is less than 75 grams:

0·2085 gave 0·5659 CO_2 and 0·1277 H_2O. $C = 74·02$; $H = 6·86$.
0·2028 „ 0·5494 CO_2 „ 0·1180 H_2O. $C = 73·86$; $H = 6·52$.
$C_{15}H_{16}O_3$ requires $C = 73·72$; $H = 6·62$ per cent.

Phenyl Glycide Ether,



$$C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CH\left<\begin{matrix}CH_2\\ |\\ O\end{matrix}\right..$$

Ninety-two and a-half grams of epichlorohydrin (1 mol.) were added to a cold solution of 94 grams of phenol (1 mol.) and 50 grams of sodium hydroxide (1¼ mols.) in 600 c.c. of water.

After twenty-four hours, the oil which had separated was extracted with ether. The ethereal solution was dried over potassium carbonate, the ether evaporated, and the residue, a slightly yellow oil, was fractionated under reduced pressure. In this way, 45 grams of an oil boiling at about 128°/15·5 mm. were obtained.

The oil thus prepared was found to contain a trace of chlorine, due possibly to the presence of a small quantity of glyceryl monochlorohydrin phenyl ether, $C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2Cl$. Considerable difficulty was experienced in removing the last traces of chlorine, but this was finally accomplished by heating for three-quarters of an hour over powdered sodium hydroxide in a water-bath and subsequently extracting with ether and fractionating in a vacuum.

The pure oil boiled at 133°/23 mm. It distils practically without decomposition at 243—244° (corr.) under atmospheric pressure:

0·2787 gave 0·7354 CO_2 and 0·1618 H_2O. $C = 71·96$; $H = 6·50$.
0·2222 „ 0·5859 CO_2 „ 0·1332 H_2O. $C = 71·91$; $H = 6·72$.
$C_9H_{10}O_2$ requires $C = 71·95$; $H = 6·73$ per cent.

The residue left in the distilling flask after the phenyl glycide ether had passed over was dissolved in hot alcohol, and from this solution about 7·5 grams of crystalline glyceryl diphenyl ether separated on cooling.

Action of Phenyl Glycide Ether on a Cold Solution of Phenol in Aqueous Potassium Hydroxide.

Four grams of phenol were dissolved in 10 c.c. of a solution of potassium hydroxide containing about 2·5 grams, and 2·28 grams of phenyl glycide ether were added to the cold solution. The mixture was allowed to stand for six days with occasional shaking. The oil had then changed almost completely into a mass of crystals; steam was now passed through to remove any unchanged phenyl glycide ether, and the solid product obtained on cooling was crystallised from alcohol. The crystals obtained weighed 3·04 grams and melted at 81—82°. The yield is thus 82 per cent. of that required by theory.

Action of Phenyl Glycide Ether on a Hot Alcoholic Solution of Phenol and Sodium Ethoxide.

Six grams of phenol and 0·2 gram of sodium were dissolved in 25 c.c. of alcohol, 2·18 grams of phenyl glycide ether were added, and the mixture was heated on a water-bath under reflux for fifteen hours. The bulk of the alcohol was then distilled off, and water and potassium hydroxide were added. The solid substance which separated was collected, washed, and drained. It was then dissolved in ether, and the ethereal solution was shaken several times with potassium hydroxide to ensure complete removal of the excess of phenol. After evaporation of the ether, the product was crystallised from alcohol. The melting point of the crystals was 80°, and the yield was 3·03 grams or 85·5 per cent. of the theoretical.

Action of Phosphorus Pentachloride on Phenyl Glycide Ether. Preparation of Phenoxydichloropropane, $C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CHCl{\cdot}CH_2Cl$.

Twenty grams of phenyl glycide ether were dissolved in 50 grams of chloroform, and the solution added by means of a tap-funnel to 40 grams of phosphorus pentachloride contained in a flask provided with a reflux condenser and cooled in a water-bath. The action is energetic at first. After all the solution had been added, the flask was warmed in the water-bath for some time. The mixture was then cooled, and treated with water and potassium hydroxide until alkaline; the chloroform was distilled off, and the residue extracted with ether. The ethereal solution was dried over potassium carbonate, and the slightly yellow oil obtained on evaporation of the ether was fractionated in a vacuum. Seventeen grams of a colourless, highly refractive oil boiling at 139—140°/13 mm. were obtained. The yield was thus 63 per cent. of that theoretically possible:

0·3731 gave 0·7260 CO_2 and 0·1728 H_2O. C = 53·07; H = 5·18.
0·2335 „ 0·4511 CO_2 „ 0·1048 H_2O. C = 52·69; H = 5·02.
0·2363 „ 0·3261 AgCl. Cl = 34·12.
0·2716 „ 0·3801 AgCl. Cl = 34·60.
$C_9H_{10}OCl_2$ requires C = 52·70; H = 4·91; Cl = 34·58 per cent.

CHEMICAL DEPARTMENT,
HARTLEY UNIVERSITY COLLEGE,
SOUTHAMPTON.

LXXVIII.—*Constitution of Hydroxyazo-compounds. Action of Diazomethane and of Mercuric Acetate.*

By CLARENCE SMITH [and, in part, ALEC DUNCAN MITCHELL].

THE protracted discussion of the constitution of hydroxyazo-compounds, which has been nearly quiescent since 1902, has within the last two years been renewed vigorously, mainly in consequence of a paper by Goldschmidt and Löw-Beer (*Ber.*, 1905, **38**, 1098). In the year mentioned, the results of the researches of numerous investigators, extending over a period of nearly twenty years, had led to the view, more or less generally accepted, that *p*-hydroxyazo-compounds and the ethers of both series possessed the azo-structure HO·R·N:N·R′, whilst *o*-hydroxyazo-compounds and their acyl derivatives were quinonehydrazones, O:R:N·NHR′. This view has been supported by the spectrometric observations of Tuck (Trans., 1907, **91**, 449). Recent researches have shown, however, that all *o*-hydroxyazo-compounds and their derivatives possess the structure implied in their name, and, in the light of these researches, the authors venture to think that Tuck's observations point to the same conclusion, the shape of the absorption curve of, for example, benzoylbenzeneazo-*p*-cresol bearing a much closer resemblance to that of benzeneazophenol than to that of benzoquinonebenzoylphenylhydrazone.

Goldschmidt and Löw-Beer (*loc. cit.*) re-examined the behaviour of *o*-hydroxyazo-compounds with phenylcarbimide, and found that these substances in the solid state at the ordinary temperature react exactly as do the para-compounds in hot benzene (Goldschmidt and Rosell, *Ber.*, 1890, **23**, 489). Goldschmidt has consequently modified his former views, and attributes the azo-structure, not only to *o*-hydroxyazo-compounds, but also to their acyl derivatives, since the formation of acetanilide as one of the products of the reductive fission of acetylbenzeneazo-*p*-cresol (Goldschmidt and Brubacher, *Ber.*, 1891, **24**, 2300) can, without the assumption of the quinonehydrazone formula, be explained by the researches of Auwers and his collaborators on the mobility of acyl groups in the esters of *o*-hydroxybenzylidenephenylhydrazones (*Ber.*, 1904, **37**, 3903, 3905, 3915, 3929, 3937).

In the same communication, Goldschmidt and Löw-Beer assert that McPherson's β-naphthaquinonebenzoylphenylhydrazone (*Amer. Chem. J.*, 1899, **22**, 364) must be an *O*-ester, in spite of its method of formation, since it behaves on reduction like the acyl derivatives of the para-series, yielding a hydrazo-compound insoluble in alkalis. The same conclusion has been reached by Auwers (*Ber.*, 1907, **40**, 2154; 1908, **41**, 403, 415), whose experiments show that *N*-acylated derivatives of *o*-hydroxyazo-compounds are too labile to exist as such, and consequently change into the isomeric *O*-esters. The labile character of the *N*-acyl derivatives of *p*-hydroxyazo-compounds has been proved by Willstätter and Veraguth (*Ber.*, 1907, **40**, 1432), who have converted McPherson's benzoquinoneacylphenylhydrazones (*Ber.*, 1895, **28**, 2414) into the *O*-esters obtained by direct acylation of the hydroxyazo-compound. Willstätter and Auwers both point out that, since the heavy acyl group wanders with such facility from the nitrogen to the oxygen atom, much more so will the light hydrogen atom of the parent hydroxyazo-compound, and therefore the latter, even when obtained from a quinone and phenylhydrazine, has the azo-structure.

It is evident from the preceding discussion that any attempt to ascertain the structure of hydroxyazo-compounds by chemical means necessitates the use of reagents unlikely to induce tautomeric change. For this reason, diazomethane and, at the suggestion of Dr. Hewitt, mercuric acetate have been selected.

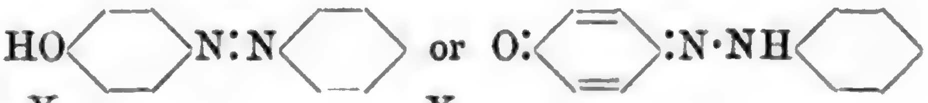
Diazomethane in cold ethereal or benzene solution reacts readily with *p*-hydroxyazo-compounds, forming the methyl ethers obtained by the ordinary methods of alkylation. There is no doubt therefore that *p*-hydroxyazo-compounds contain a hydroxyl group and have the azo-structure.

Diazomethane does not react with *o*-hydroxyazo-compounds, a result which seems to prove the absence of a hydroxyl group in these substances. The proof is, however, inconclusive, for were the formulæ of the *o*-hydroxyazo-compounds of the quinonehydrazone type, one would expect to obtain the *N*-methyl ether, and, moreover, diazomethane is not an infallible reagent for the detection of the hydroxyl group. It does not react with methyl or ethyl alcohol, and von Pechmann points out that it has only a slight tendency to react with weakly acidic substances (*Ber.*, 1895, **28**, 1624). The *o*-hydroxyazo-compounds are undoubtedly much weaker acids than the para-compounds,* and the effect of this property added to that of the screening influence of the large azo-complex in the ortho-position with respect to the hydroxyl group may very well be the cause of the non-reactivity of diazomethane with *o*-hydroxyazo-compounds.

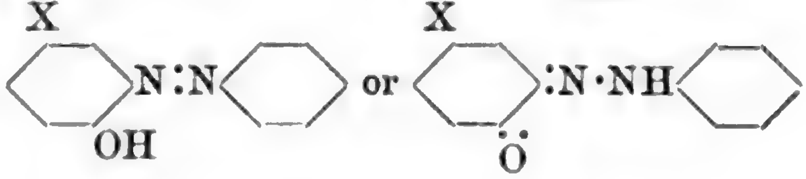
That the reactivity of *o*-hydroxyazo-compounds is affected by steric influences is proved by their behaviour on alkylation. Whereas ethers result by the simple addition of methyl sulphate to the alkaline solution of a *p*-hydroxyazo-compound, members of the ortho-series require heating before alkylation occurs. These results had been established by one of the authors, who was forestalled in the publication by Colombano (*Atti R. Accad. Lincei*, 1907, [v], **16**, ii, 457). Ethers of *o*-hydroxyazo-compounds are obtained readily from the silver salt and an alkyl iodide, a result which is analogous to that observed by V. Meyer in the esterification of *o*-*o*-disubstituted benzoic acids.

The introduction of mercury into aromatic nuclei has been accomplished by several investigators, particularly by Dimroth (*Ber.*, 1898, **31**, 2154; 1899, **32**, 758; 1902, **35**, 2032), who has shown that amines and phenols react readily with mercuric acetate, one or more mercuriacetate groups entering the ortho- and para-positions with respect to the amino- or hydroxyl-group, but never in the meta-position. These results seem to offer a satisfactory method for the determination of the constitution of hydroxyazo-compounds. According as their structure is represented by:

I. Para-series:



II. Ortho-series:



the mercuriacetate complex will enter the phenolic or the aminic nucleus. In the former case, two groups at most can be introduced, whilst in the quinonehydrazone the possibility exists for the entry of three complexes. The behaviour of benzeneazophenol, 2:4:6-tribromobenzeneazophenol, benzeneazo-*o*-nitrophenol, benzeneazo-*o*-*o*-dibromophenol, benzeneazo-*p*-cresol, and benzeneazo-*m*-bromo-*p*-cresol respectively with mercuric acetate in hot aqueous-alcoholic solution has been examined, with the result that in both the para- and the ortho-series the number of mercuriacetate groups entering the molecule of the hydroxyazo-compound is equal to the number of unsubstituted positions ortho to the oxygen atom. It appears strange, at first sight, that mercuric acetate does not attack substances such as benzeneazo-*o*-*o*-dibromophenol and benzeneazo-*m*-bromo-*p*-cresol; one would expect the salt to attack the unsubstituted phenyl radicle, $\dot{:}N\cdot C_6H_5$. In reality, this non-reactivity furnishes a strong argument in favour of the azo-structure of hydroxyazo-compounds, for azobenzene, in which occurs the same group, $\dot{:}N\cdot C_6H_5$, is quite unaffected by mercuric acetate, whereas substances, such as acetanilide and diphenylamine, containing the group $\cdot NH\cdot C_6H_5$, which would be present in hydroxyazo-compounds were they quinonehydrazones, react very readily. Unfortunately, mercuric acetate acts simply as an oxidising agent on benzylidenephenylhydrazone, the structure of which somewhat resembles that of a quinonehydrazone.

---

* This will form the subject of a future communication.

The identical behaviour of *o*- and *p*-hydroxyazo-compounds with mercuric acetate must be conditioned by similarity in structure, and the compounds of the ortho-series must therefore be of the azo-type, since all evidence, chemical or physical, proves that the para-compounds are not quinonehydrazones.

EXPERIMENTAL.

Diazomethane and Benzeneazophenol.

Half a gram of well-dried benzeneazophenol was added to the benzene solution of diazomethane obtained from 5 c.c. of nitrosomethylurethane. The hydroxyazo-compound dissolved with vigorous effervescence, which ceased after thirty minutes. The greater part of the solvent was removed by distillation, and the residual liquid was washed with dilute sodium hydroxide until the filtrate was practically colourless, then with water, dried over calcium chloride, and evaporated. The residual red oil solidified to orange-red crystals, which, after recrystallisation from light petroleum, melted at 53°. A mixture of the substance and benzeneazoanisole melted at the same temperature:

0·0862 gave 0·2332 CO_2 and 0·0462 H_2O. C = 73·77; H = 5·95.

$C_{13}H_{12}ON_2$ requires C = 73·59; H = 5·66 per cent.

Diazomethane and Benzeneazo-α-naphthol.

When 1 gram of well-dried benzeneazo-α-naphthol was added to the ethereal solution of diazomethane from 5 c.c. of nitrosomethylurethane, a vigorous effervescence occurred, which lasted one hour. After being washed with potassium hydroxide and with water, the ethereal solution was dried over calcium chloride and evaporated.

The residue weighed 0·7 gram, and, after two crystallisations from methyl alcohol, melted at 82°, the melting point being unchanged by the addition of benzeneazo-α-naphthyl methyl ether:

0·0738 gave 0·2110 CO_2 and 0·0346 H_2O. C = 77·97; H = 5·21.
$C_{17}H_{14}ON_2$ requires C = 77·86; H = 5·34 per cent.

Diazomethane and Benzeneazo-p-*cresol.*

One gram of benzeneazo-*p*-cresol was added to the ethereal solution of diazomethane from 5 c.c. of nitrosomethylurethane. The solution effervesced gently for five hours, but, after evaporating the solution to a small volume, the fine ruby-red needles which separated melted at 106°, and the melting point was unchanged by the addition of benzeneazo-*p*-cresol.

p-*Chlorobenzeneazo*-p-*cresyl Methyl Ether*, $C_6H_4Cl·N_2·C_7H_6·O·CH_3$.

(I) Five grams of the hydroxyazo-compound were suspended in 100 c.c. of alcohol, and treated with a slight excess of 40 per cent. potassium hydroxide. The intensely red solution was heated until solution was complete, and then an excess of aqueous silver nitrate was added. The purple precipitate of the silver salt was collected, washed with hot alcohol, boiling water, and again with alcohol, dried, suspended in methyl alcohol, and treated with an excess of methyl iodide. By heating on the water-bath, the reaction was completed; after removing the silver iodide, the filtrate was evaporated to a small bulk. The reddish-yellow crystals which separated from the cold solution were collected, washed with methyl alcohol, and dried. By recrystallisation from methyl alcohol, the ether was obtained in orange-red needles melting at 68°:

0·1588 gave 0·3741 CO_2 and 0·0706 H_2O. C = 64·25; H = 4·94.
$C_{14}H_{13}ON_2Cl$ requires C = 64·49; H = 4·99 per cent.

The yield was about 84 per cent. of the theoretical.

(II) The same ether was obtained when a solution of 2 grams of methyl iodide and 2·5 grams of *p*-chlorobenzeneazo-*p*-cresol, in 30 c.c. of methyl alcohol containing 0·3 gram of sodium, was heated on the water-bath for six hours. A hot 20 per cent. aqueous solution of potassium hydroxide was then added until a turbidity formed. The precipitate was separated from the cold solution, washed with alcohol and water, and dried. By recrystallisation from methyl alcohol, orange-red needles of the preceding ether were obtained, which melted at 68°.

Diazomethane and p-*Chlorobenzeneazo*-p-*cresol.*

One gram of the hydroxyazo-compound was added to the ethereal solution of diazomethane obtained from 5 c.c. of nitrosomethylurethane. A gentle effervescence lasting for one and a-half hours was observed, at the conclusion of which the solution was concentrated by evaporation, whereby reddish-yellow leaflets of the original hydroxyazo-compound were obtained melting at 153°, the melting point being unchanged by the addition of *p*-chlorobenzeneazo-*p*-cresol.

In order to ascertain whether a reaction occurs at a higher temperature, 0·5 gram of *p*-chlorobenzeneazo-*p*-cresol and a solution of diazomethane (from 2·5 c.c. of nitrosomethylurethane) in benzene were heated at 100° for two hours in a sealed tube. The diazomethane had all decomposed, but, after evaporation of the solvent, the residue melted at 152—153°, and the melting point was unchanged by the addition of the original hydroxyazo-compound.

Diazomethane and β-Benzeneazo-α-naphthol.

One gram of the hydroxyazo-compound and the ethereal solution of diazomethane from 5 c.c. of nitrosomethylurethane were kept in a closed vessel for several weeks. By evaporation of the solvent, dark red needles were obtained which melted at 132—134°. The melting point was raised to 138° by one recrystallisation of the substance from methyl alcohol, and remained unchanged by the addition of β-benzeneazo-α-naphthol.

Mercuric Acetate and Azobenzene.

A solution of 6 grams of mercuric acetate in 20 c.c. of water and 3 c.c. of acetic acid was added to 4 grams of azobenzene dissolved in 200 c.c. of alcohol. The mixture was heated for six hours on the water-bath. A small quantity, 0·7 gram, of mercuric acetate separated from the cold solution. This was removed, and the filtrate evaporated to 50 c.c. and added to 150 c.c. of water. A red, crystalline solid, weighing 4 grams and melting at 65—66°, was obtained, which, after recrystallisation from alcohol, melted at 68°. The melting point was unchanged when the substance was mixed with azobenzene:

0·3000 gave 32 c.c. nitrogen at 15° and 739 mm. N = 15·38.

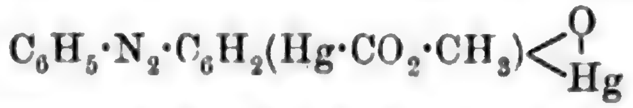
$C_{12}H_{10}N_2$ requires N = 15·38 per cent.

Benzeneazophenol Dimercuriacetate.

A solution of 32 grams of mercuric acetate in 150 c.c. of water and 20 c.c. of acetic acid was added to 10 grams of benzeneazophenol dissolved in 300 c.c. of alcohol, and the clear blood-red mixture was heated for six hours on the water-bath. The bulky, orange-yellow precipitate which had separated was collected, washed with hot dilute acetic acid, water, and alcohol, and dried at 110°. During the drying, the substance gave off acetic acid and contracted to small, hard, red, nodules. The yield was nearly quantitative.

The substance was purified by adding its solution in 150 c.c. of boiling glacial acetic acid to 400 c.c. of alcohol. The orange-yellow precipitate was washed with dilute acetic acid, alcohol, and ether, and dried as rapidly as possible at the ordinary temperature. The substance continuously decreased in weight, owing to loss of acetic acid:

0·3687 gave 0·2126 Hg. Hg = 57·6.
0·7632 „ 26·6 c.c. of nitrogen at 17° and 749·5 mm. N = 4·0.
$C_{16}H_{14}O_5N_2Hg_2$ requires Hg = 56·0; N = 3·9 per cent.
0·4326 at 120° lost 0·0257. Loss = 5·9.
Theoretical loss for 1 mol. $C_2H_4O_2$ = 8·4 per cent.

The analyses show that the benzeneazophenol dimercuriacetate had already lost a considerable amount of acetic acid. Since many other attempts to obtain the pure dry dimercuriacetate were unsuccessful, the substance was dried at 120°, the composition being then represented by the formula  $C_6H_5\cdot N_2\cdot C_6H_2(Hg\cdot CO_2\cdot CH_3){<}\begin{smallmatrix}O\\ |\\ Hg\end{smallmatrix}$:

0·3219 gave 11·7 c.c. of nitrogen at 20° and 763 mm. N = 4·2.
0·4902 „ 0·3004 Hg. Hg = 61·3.
$C_{14}H_{10}O_3N_2Hg$ requires N = 4·3; Hg = 61·2 per cent.

The dried substance is a yellowish-brown powder, which darkens continuously on heating, but is not melted at 300°. It is insoluble in hot water and very sparingly soluble in alcohol, chloroform, ethyl acetate or benzoate, benzene, and nitrobenzene; it is moderately soluble in pyridine, and dissolves readily in glacial acetic acid.

Benzeneazophenol Dimercurichloride, $C_6H_5\cdot N_2\cdot C_6H_2(HgCl)_2\cdot OH$.

Five grams of the compound just described were boiled with 200 c.c. of 5 per cent. aqueous potassium hydroxide, and the hot filtered solution treated with 200 c.c. of a saturated solution of sodium chloride. The orange-red precipitate was collected, washed with water, and digested with dilute hydrochloric acid, whereby the colour changed to brick-red. The precipitate was collected, washed with hot water and alcohol, and dried at 110°. The weight was 4 grams:

0·2158 gave 0·0923 AgCl and 0·1500 HgS. Cl = 10·6; Hg = 59·9.
0·5010 „ 17·8 c.c. of nitrogen at 16° and 760 mm. N = 4·2.
$C_{12}H_8ON_2Cl_2Hg_2$ requires Cl = 10·6; Hg = 60·0; N = 4·2 per cent.

The *dimercurichloride* is a dull red, amorphous powder, which does not melt below 300°, and is insoluble, or nearly so, in the usual solvents. Attempts to obtain from it 2 : 4 : 6-trisbenzeneazophenol by the action of diazobenzene chloride were unsuccessful, probably owing to the slight solubility of the dimercurichloride in alkali hydroxides.

Benzeneazophenol dimercuribromide, $C_6H_5 \cdot N_2 \cdot C_6H_2(HgBr)_2 \cdot OH$, was best obtained by treating a solution of the dimercuriacetate in glacial acetic acid with a few c.c. of a hot concentrated solution of potassium bromide. The brownish-red precipitate was filtered from the hot liquid, washed with boiling water and alcohol, boiled with glacial acetic acid to extract traces of unchanged dimercuriacetate, again filtered and washed, and finally dried at 110°. It is a brownish-red powder, which does not melt below 300°, and is practically insoluble in the usual solvents:

0·4208 gave 0·2092 AgBr. Br = 21·15.

$C_{12}H_8ON_2Br_2Hg_2$ requires Br = 21·2 per cent.

Attempts to replace the mercuribromide groups by bromine did not lead to definite results.

Mercuric Acetate and Benzeneazo-o-o-dibromophenol.

A solution of 3·5 grams of mercuric acetate in 15 c.c. of water and 1 c.c. of acetic acid was added to 3·5 grams of the hydroxyazo-compound dissolved in 200 c.c. of alcohol and the mixture heated for six hours on the water-bath. The small precipitate (0·5 gram) which had separated from the cold solution was recrystallised from acetic acid, and thus obtained in faintly yellow needles; it did not contain nitrogen or bromine, and was not further examined.

The solution was evaporated to 40 c.c. and poured into water. The yellowish-brown precipitate was collected, washed, and dried. It weighed 3 grams, and melted at 135—136°; its identity with benzeneazo-*o*-*o*-dibromophenol was confirmed by a mixed melting-point determination.

2 : 4 : 6-*Tribromobenzeneazophenol Dimercuriacetate*, $C_6H_2Br_3 \cdot N_2 \cdot C_6H_2(Hg \cdot CO_2 \cdot CH_3)_2 \cdot OH$.

Six grams (2 mols.) of mercuric acetate dissolved in 20 c.c. of water and 1 c.c. of acetic acid were added to the solution of 4 grams (1 mol.) of the hydroxyazo-compound in 200 c.c. of alcohol. After the mixture had been heated for six hours on the water-bath, the pinkish-red precipitate which had separated was collected. Another ½ gram of precipitate was obtained by concentrating the filtrate to 20 c.c. The combined precipitates were washed with dilute acetic acid and water and dried, the weight then being 6·5 grams. The substance was recrystallised from glacial acetic acid, and the pale red, microcrystalline powder thus obtained was washed with alcohol and dried at the ordinary temperature:

0·3175 gave 0·2295 CO_2 and 0·0293 H_2O. C = 19·7; H = 1·0.
0·3091 „ 0·1298 Hg „ 0·1854 AgBr. Hg = 42·0; Br = 25·5.
0·2615 „ 6·2 c.c. nitrogen at 18° and 739 mm. N = 2·7.
$C_{16}H_{11}O_5N_2Br_3Hg_2$ requires C = 20·2; H = 1·15; Hg = 42·1; Br = 25·2; N = 2·9 per cent.

Tribromobenzeneazophenol dimercuriacetate, which does not melt below 300° and is very sparingly soluble in the usual solvents with the exception of glacial acetic acid, is more stable than benzeneazophenol dimercuriacetate, but loses acetic acid at 120°:

0·3865 lost 0·0240. Theoretical loss for 1 mol. $C_2H_4O_2$ = 0·0244. By prolonged heating at 120°, mercury is eliminated.

Benzeneazo-o-nitrophenol Mercuriacetate, $C_6H_5\cdot N_2\cdot C_6H_2(NO_2)(Hg\cdot CO_2\cdot CH_3)\cdot OH$.

A solution containing 5 grams of mercuric acetate in 30 c.c. of water and 2 c.c. of acetic acid was added to a hot solution of 2·4 grams of benzeneazo-*o*-nitrophenol in 250 c.c. of alcohol, and the mixture heated for six hours on the water-bath. The precipitate was filtered from the cold solution, washed with alcohol and hot water, and recrystallised from glacial acetic acid. It was obtained as a pale yellow, microcrystalline powder, which did not melt below 300°, and was insoluble, or nearly so, in the usual solvents, excepting acetic acid:

0·3008 gave 22·0 c.c. of nitrogen at 15° and 750 mm. N = 8·4.
0·2564 „ 0·1028 Hg. Hg = 40·1.
$C_{14}H_{11}O_5N_3Hg$ requires N = 8·4; Hg = 39·9 per cent.

Benzeneazo-o-nitrophenol mercuribromide,
$C_6H_5\cdot N_2\cdot C_6H_2(NO_2)(HgBr)\cdot OH$,
was obtained as a pale yellow precipitate by adding a concentrated solution of potassium bromide to the mercuriacetate dissolved in glacial acetic acid. The precipitate was washed with hot water and dried:

0·4201 gave 0·1460 AgBr. Br = 14·8.
$C_{12}H_8O_3N_3BrHg$ requires Br = 15·3 per cent.

*Benzeneazo-*p*-cresol Mercuriacetate,* $C_6H_5\cdot N_2\cdot C_7H_5(OH)\cdot Hg\cdot CO_2\cdot CH_3$.

A solution of 32 grams (2 mols.) of mercuric acetate in 230 c.c. of water and 5 c.c. of acetic acid was added to the boiling solution of 10 grams of benzeneazo-*p*-cresol in 600 c.c. of alcohol; the mixture was heated for seven hours on the water-bath. A voluminous red precipitate separated, which was collected, washed with alcohol, dilute acetic acid, and hot water; after being dried, it weighed 18·5 grams. The purification can be effected by repeated crystallisation from glacial acetic acid, but the following method was employed with a saving of time and of material. The crude product was dissolved in boiling glacial acetic acid, and by the addition of a small quantity of hot water a slight precipitate formed, which was removed and neglected. The bulk of the substance left in the solution was precipitated by excess of water, and, after being dried, treated in the same way as before. The precipitate obtained in this second treatment was finally crystallised from glacial acetic acid. It separated in reddish-brown needles, was very sparingly soluble in the usual solvents, excepting acetic acid, and darkened on heating, melting with decomposition at 269—270°. These are the properties of benzeneazo-*p*-cresol mercuriacetate obtained by Dimroth (*Ber.*, 1902, **35**, 2864) from diazobenzene chloride and *p*-cresol-*m*-mercuriacetate (Me : OH = 1 : 4), and the identity of the two substances was proved by a mixed melting-point determination:

0·9868 gave 0·4159 Hg. Hg = 42·15.
0·3012 „ 15·8 c.c. of nitrogen at 15° and 768 mm. N = 6·2.
$C_{15}H_{14}O_3N_2Hg$ requires Hg = 42·55; N = 6·0 per cent.

*Benzeneazo-*p*-cresol mercurichloride,* $C_6H_5\cdot N_2\cdot C_7H_5(OH)\cdot HgCl$, was obtained by adding 40 c.c. of a saturated salt solution to 3 grams of the mercuriacetate dissolved in 20 c.c. of acetic acid. The precipitate was collected, washed, and recrystallised twice from a large volume of alcohol, whereby it was obtained in yellowish-brown needles, which darkened on heating, and melted and decomposed at 246—248° (Dimroth: 249° with decomposition):

0·3588 gave 0·1616 Hg and 0·1176 AgCl. Hg = 45·0; Cl = 8·1.
$C_{13}H_{11}ON_2ClHg$ requires Hg = 44·8; Cl = 7·95 per cent.

*Mercuric Acetate and Benzeneazo-*m*-bromo-*p*-cresol.*

A solution of 3·2 grams of mercuric acetate in 5 c.c. of water and a few drops of acetic acid was added to 1·5 grams of the hydroxyazo-compound dissolved in 50 c.c. of alcohol, and the mixture was heated on the water-bath for six hours. The precipitate, separated from the cold filtrate, weighed 1 gram, and 0·4 gram was obtained by concentrating the mother liquor. The total amount was recrystallised from acetic acid. The red crystals melted at 120—121°, and the melting point was unchanged by admixture with benzeneazo-*m*-bromo-*p*-cresol (Me : OH = 1 : 4) (m. p. 123° corr.):

0·1061 gave 9·2 c.c. of nitrogen at 18·5° and 742·5 mm. N = 9·8.

$C_{13}H_{11}ON_2Br$ requires N = 9·6 per cent.

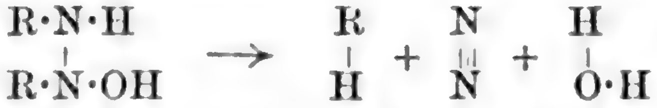
The expenses of this investigation have been partly defrayed by a grant from the Research Fund of the Chemical Society, for which the authors desire to express their thanks.

East London College.

LXXIX.—*The Quantitative Conversion of Aromatic Hydrazines into Diazonium Salts.*

By Frederick Daniel Chattaway.

The primary aromatic hydrazines, which are so readily obtained from diazonium salts by reduction, might be expected to be reconverted into the latter with similar ease by oxidation. This reconversion, however, has proved to be a matter of great difficulty. For it to take place, two hydrogen atoms of the $\cdot NH\cdot NH_2$ group must be replaced by hydroxyl groups, and, as the author has recently shown (Trans., 1907, **91**, 1323; 1908, **93**, 270), when one such group has been introduced the typical diazo-decomposition:



$$\begin{array}{c}\mathrm{R\cdot N\cdot H}\\ |\\ \mathrm{R\cdot N\cdot OH}\end{array} \longrightarrow \begin{array}{c}\mathrm{R}\\ |\\ \mathrm{H}\end{array} + \begin{array}{c}\mathrm{N}\\ |||\\ \mathrm{N}\end{array} + \begin{array}{c}\mathrm{H}\\ |\\ \mathrm{O\cdot H}\end{array}$$

occurs so readily that even in presence of acids comparatively insignificant amounts of diazonium salts are formed, whilst in presence of alkalis they are not produced at all.

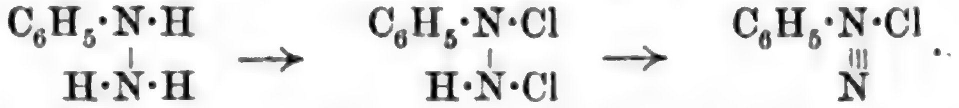
Emil Fischer (*Annalen*, 1877, **190**, 97) first showed that the reaction was possible, and recognised the presence of a diazonium salt among the products of the oxidation of phenylhydrazine sulphate by yellow mercuric oxide. The amount which can be thus formed is, however, very small, and, although Altschul (*J. pr. Chem.*, 1896, [ii], **54**, 496) found that a much larger yield could be obtained by employing nitrous acid as the oxidising agent, no really satisfactory method of effecting the reconversion has yet been described.

The author finds that all primary aromatic hydrazines can be quantitatively converted into the corresponding diazonium salts either by chlorine or by bromine.*

If either halogen is allowed to act at a low temperature on the hydrazine dissolved in alcohol, the diazonium salt separates out in a pure state.

Unless, however, the solid salt is required, the operation can be more easily carried out by dissolving the hydrazine in glacial acetic acid, cooling the solution to about – 15° by addition of crushed ice, and either passing in a rapid stream of chlorine or adding the calculated quantity of bromine dissolved in acetic acid and similarly cooled by ice.

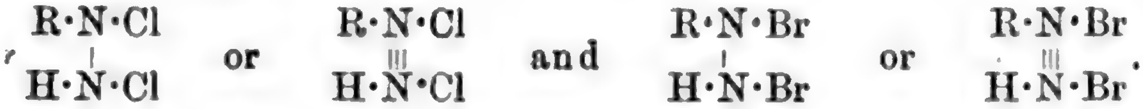
The formation of the solid diazonium salt is without doubt due to a substitution by halogen of two atoms of hydrogen in the $\cdot NH\cdot NH_2$ group, followed by the elimination of halogen acid, thus:



$$\begin{array}{c} C_6H_5\cdot N\cdot H \\ | \\ H\cdot N\cdot H \end{array} \longrightarrow \begin{array}{c} C_6H_5\cdot N\cdot Cl \\ | \\ H\cdot N\cdot Cl \end{array} \longrightarrow \begin{array}{c} C_6H_5\cdot N\cdot Cl \\ ||| \\ N \end{array}.$$

As in other cases where hydrogen attached to nitrogen is replaced by halogen, an additive product is probably first formed, in this instance by the addition of four halogen atoms, each nitrogen atom thus becoming quinquevalent. The successive elimination of three molecules of halogen acid then gives rise to the diazonium salt.

It seems probable that the removal of the last molecule of halogen acid, which is necessary for formation of the solid diazonium compounds, only takes place when the latter assume the solid state, and that when these compounds exist in solution or undergo any of the reactions which are characteristic of them they actually have the structure:



$$\begin{array}{c} R\cdot N\cdot Cl \\ | \\ H\cdot N\cdot Cl \end{array} \text{ or } \begin{array}{c} R\cdot N\cdot Cl \\ ||| \\ H\cdot N\cdot Cl \end{array} \text{ and } \begin{array}{c} R\cdot N\cdot Br \\ | \\ H\cdot N\cdot Br \end{array} \text{ or } \begin{array}{c} R\cdot N\cdot Br \\ ||| \\ H\cdot N\cdot Br \end{array}.$$

The relationship of the diazonium salts to the hydrazines and all their reactions can be better explained on this hypothesis than on any other.

Action of Chlorine on Phenylhydrazine.

When chlorine is passed rapidly into a solution of phenylhydrazine kept at a low temperature, action at once takes place; hydrogen is replaced by chlorine and hydrogen chloride is produced, but no nitrogen is evolved, nor does any substitution in the ring take place, benzenediazonium chloride and hydrogen chloride being the sole products.

---

* A large number of totally different products can be obtained from primary aromatic hydrazines by the action on them of the halogens according to the conditions under which the action takes place. A full treatment of the subject is reserved for a later communication; in this paper, the production of diazonium salts is alone dealt with.

If solid benzenediazonium chloride is to be prepared, it is best to operate in alcoholic solution, cooling with solid carbon dioxide, but if the salt is not required in the solid form the action can be much more easily carried out in acetic acid solution.

To prepare the solid diazonium salt, 5 grams of phenylhydrazine, freshly distilled and twice recrystallised, were dissolved in 100 c.c. of absolute alcohol, and cooled strongly by the addition of solid carbon dioxide, so much of the latter being added that a pasty mass was obtained. Through this a rapid stream of dry chlorine was passed until the whole was saturated, the semi-liquid mass being thoroughly stirred during the passage of the gas by the delivery tube. The liquid became pale yellow, and benzenediazonium chloride separated as a white solid. One hundred c.c. of dry ether, also strongly cooled and containing suspended solid carbon dioxide, were added, and a rapid current of dry air was aspirated through the mixture until the excess of chlorine and the solid carbon dioxide had been removed and the temperature of the liquid had risen to about $-20°$. The solid benzenediazonium chloride was then filtered off and well washed with dry ether.

The purity of the substance was established by a chlorine estimation, and also by converting it into benzeneazo-β-naphthol by coupling it with β-naphthol. The benzeneazo-β-naphthol thus obtained crystallised from alcohol in brilliant scarlet needles melting at 135°, and was identical with a specimen prepared from benzenediazonium chloride prepared by diazotising aniline.

To prepare an acetic acid solution of the diazonium salt, 2·16 grams of phenylhydrazine, purified as before, were dissolved in 80 c.c. of glacial acetic acid and 40 grams of crushed ice added. A rapid stream of chlorine was passed through the liquid, stirring as before, until it was saturated and the gas escaped freely. No nitrogen was evolved, the action taking place quietly and quantitatively. The liquid at first assumed a slightly red tint, which, however, disappeared as the passage of the chlorine was continued, a pale yellow liquid being finally obtained. To remove the excess of chlorine, more crushed ice was added, and air was drawn through the liquid until the odour of chlorine could not be detected. The benzenediazonium chloride produced was then estimated by conversion into benzeneazo-β-naphthol,* a quantitative yield of which, in a perfectly pure state, can be obtained in a carefully conducted experiment.

It is thus seen that no substitution in the benzene nucleus occurs under the conditions named, the sole product of the action of chlorine on phenylhydrazine being benzenediazonium chloride, which is produced in theoretical amount.

---

* A number of experiments made with weighed quantities of pure diazonium compounds showed that accurate results could be obtained by filtering off the azo-compound in a Gooch crucible and drying at 110°.

Action of Bromine on Phenylhydrazine.

The action of bromine on phenylhydrazine is exactly similar to that of chlorine, benzenediazonium bromide and hydrogen bromide alone being produced. Since the amount of bromine required can be accurately weighed, the operations are more easily carried out.

4·32 Grams of pure phenylhydrazine were dissolved in 50 c.c. of absolute alcohol and cooled by solid carbon dioxide, the latter being added in excess so as to form a semi-solid mass; 12·8 grams of bromine were next mixed with 50 c.c. of absolute alcohol, similarly cooled and containing an excess of suspended solid carbon dioxide. The liquid containing the bromine was then quickly added to that containing the phenylhydrazine, and the two thoroughly stirred together. The mixture became pale yellow, and solid benzenediazonium bromide separated; 100 c.c. of dry ether were next added, and a current of air aspirated through the mixture, this being continued until the solid carbon dioxide had disappeared and the temperature had risen to about − 20°. The benzenediazonium bromide was then filtered off and washed with dry ether. It was obtained as a white, crystalline powder, which in bulk was seen to have a faint yellow tint. On adding ether gradually to a solution of the salt in cold alcohol, it separated in small, six-sided plates of a very faint yellow colour. Its purity was ascertained by a bromine estimation and by converting it as before into benzeneazo-β-naphthol.

Unless the solid salt is required, it is, however, much simpler to work in glacial acetic acid solution, cooling by crushed ice. Phenylhydrazine can be so easily and rapidly converted into diazonium bromide in this way that the operation is excellently adapted for a lecture experiment.

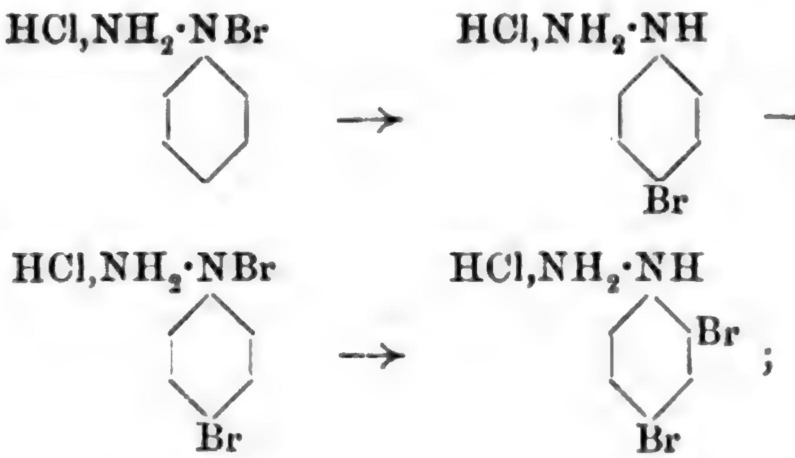
The following is a convenient procedure: 2·16 grams of pure phenylhydrazine are dissolved in 40 c.c. of acetic acid, and 20 grams of crushed ice added; 6·4 grams of bromine are dissolved in 40 c.c. of acetic acid and 20 grams of crushed ice added. The temperature of each liquid having fallen to about − 15°, the two are rapidly mixed, the bromine solution being poured into the hydrazine solution, the latter being rapidly stirred; some heat is developed, but the temperature of the whole should not rise above − 10°, as the ice still remains in excess if the operations are carried out quickly. A little benzenediazonium perbromide is formed locally where the bromine is in excess, but this at once disappears on stirring, and a clear, pale yellow liquid is obtained, no nitrogen being evolved.

The clear liquid is next poured over a considerable excess of crushed ice, and made slightly alkaline by the cautious addition of a cold concentrated solution of potassium hydroxide. On adding β-naphthol dissolved in dilute aqueous potassium hydroxide, benzeneazo-β-naphthol is thrown down as a brilliant red precipitate. The yield in a carefully conducted experiment is theoretical. In two test experiments, using the above quantity of phenylhydrazine, 4·9 and 5 grams of benzeneazo-β-naphthol were obtained, the amount which theoretically should be produced being 4·96 grams.

All primary aromatic hydrazines which have been studied are acted on by chlorine and bromine in a precisely similar manner, and the action appears to be a general one.

It may, however, again be noted that the halogens can produce from the hydrazines a great variety of substances, as the hydrogen attached to the nitrogen is substituted atom by atom, and the nitrogen halogen derivatives formed can break down or transform in many different ways, depending on the conditions. As an illustration of this, reference may be made to the observation of Michaelis (*Ber.*, 1893, **26**, 2190), confirmed by Vaubel (*J. pr. Chem.*, 1894, [ii], **49**, 540; 1897, [ii], **55**, 220), that, when phenylhydrazine or its acetyl derivative is brominated, in addition to a bromo-substituted hydrazine, a bromo-substituted diazonium salt is produced. Following up a statement made by Emil Fischer (*Annalen*, 1893, **272**, 214) that acetylphenylhydrazine can be directly brominated if dissolved in concentrated hydrochloric acid, Michaelis, by the direct action of bromine at the ordinary temperature on phenylhydrazine and acetylphenylhydrazine, prepared *p*-bromophenylhydrazine and 2 : 4-dibromophenylhydrazine, and noted that, in addition, *p*-bromo- and 2 : 4-dibromo-benzenediazonium chloride were respectively produced.

The formation of these compounds is due to the substitution of hydrogen in the imino-group of the hydrazine by bromine, the action of the halogen on the amino-group being hindered, or rendered much less rapid, by the presence of the concentrated hydrochloric acid, this by combining with the group preventing the addition of halogen which must precede substitution. The nitrogen-bromide thus formed undergoes under the influence of the halogen acid the transformation characteristic of phenyl acyl nitrogen bromides, the halogen entering the ring in the para- and ortho-positions and forming the substituted hydrazine, for example:



at each stage of this transformation a certain amount of the substituted hydrazine is acted on in the manner described in this paper and converted into the corresponding diazonium salt.

Action of Chlorine and Bromine on o- *and* p-*Tolylhydrazine,* p-*Bromophenylhydrazine,* p-*Nitrophenylhydrazine, Phenylhydrazine*-p-*sulphonic Acid, and β-Naphthylhydrazine.*

The action of chlorine and of bromine on these hydrazines has been investigated in a similar manner, and with similar results to those previously described. In every case, the action of the halogen at a low temperature converts the hydrazine into the corresponding diazonium salt.

The conversion in each of these cases is most conveniently effected by bromine carrying out the reaction in acetic acid, the amount of acid used and the details of procedure being suitably modified. In no case, if the temperature is kept low, is halogen substituted in the aromatic residue, this only occurring in presence of mineral acids when the temperature is such as to allow transformation of the mono-halogen imino-substitution product to take place.

In order to obtain a quantitative yield of diazonium salt in any of these reactions, it is necessary to work very carefully and to use accurately weighed amounts of pure bromine and recently purified hydrazine. All primary aromatic hydrazines are so readily oxidised by the oxygen of the air (Chattaway, Trans., 1907, **91**, 1323) that unless purified by distillation under diminished pressure, or recrystallised not long before use, they are certain to contain brown-coloured oxidation products. Such slightly impure hydrazines do not give a perfectly clear solution of the diazonium compound, and small quantities of brown solid, or even tarry matters, are thrown out on neutralisation. These, however, can be filtered off from the aqueous solution of the diazonium salt, the yield of the latter being slightly reduced. Working with ordinary care, however, it is easy to obtain a yield of 90—95 per cent. of the theoretical.

The author is indebted to the Government Grant Committee of the Royal Society for a grant, which has partly covered the cost of this investigation, and to Dr. H. B. Baker for allowing him to use the Christ Church laboratory.

CHRIST CHURCH,
OXFORD.

LXXX.—*Quantitative Separation of Thallium from Silver.*

By JAMES FREDERICK SPENCER and MARGARET LE PLA.

IN the course of some work on thallium compounds, we desired to effect a complete separation of silver and thallium, both for purposes of analysis and also for purification of the salts.

Several methods are to be found in the literature of the subject for effecting this separation. These methods, on trial, have proved to be either too lengthy and tedious, or not sufficiently quantitative for our purpose.

Crookes describes a method based on the precipitation of silver sulphide by means of hydrogen sulphide in acid solution. Experiment has shown that silver sulphide precipitated in presence of a thallous salt invariably contains small quantities of thallium. A second method consists in oxidising the thallium salt by means of nitrohydrochloric acid to the sesquichloride, $TlCl_3,3TlCl$, which is slightly soluble in hot water. The solution containing this is then boiled, and the silver chloride collected and washed with boiling water until all the thallium is removed. This method is extremely tedious, for thallium sesquichloride is very sparingly soluble in water, dissolving only to the extent of 3·6 grams per litre at 25°, and is still less soluble in dilute hydrochloric acid, with which the washing must be carried out. This is necessitated since thallium sesquichloride is hydrolysed by water according to the equation:

$$TlCl_3,3TlCl + 3H_2O \longrightarrow Tl(OH)_3 + 3TlCl + 3HCl.$$

Another method depends on the reduction of the iodides of the two metals by means of zinc. The mixture of iodides is allowed to stand in contact with a rod of pure zinc which reduces both iodides to metal; when all has been reduced, the excess of zinc is removed, and the thallium dissolved in dilute sulphuric acid, which will leave the silver unattacked.

This process is very good, but is long and very tedious. It depends on the iodides coming into contact with the zinc, which can only occur when they are in solution, and, since they are both very slightly soluble in water, this must be a very lengthy process.

The foregoing processes having failed to meet our needs, we adopted the following method, which we have found to be quantitative, and easily and quickly carried out.

The mixture of silver and thallium salts is treated in the presence of about 50 c.c. of water with a rapid stream of chlorine. By this means, the thallium is converted into a thallic salt in a very few minutes, the silver being precipitated as chloride. Thallic chloride, being extremely soluble in water, is filtered from the silver chloride, reduced by sulphur dioxide, precipitated as thallous iodide, and estimated in the usual way. An attempt was made to substitute the chlorine by bromine, but the results obtained showed that the oxidation of the thallium was incomplete. An attempt was also made to determine the thallium directly in the thallic condition, and so avoid the reduction by sulphur dioxide. The thallium was therefore precipitated, after removal of the silver, by ammonia, the hydroxide filtered off, dried at 120°, and weighed. The results, however, showed that the dried precipitate was not a homogeneous compound.

EXPERIMENTAL.

I. *Separation of Silver and Thallium.*

Solutions of thallous nitrate and silver nitrate of known composition were prepared from pure salts supplied by Kahlbaum; these were then analysed in the following manner.

Chlorine was passed through the solution for about ten minutes, whereby the thallous salt was completely oxidised to a thallic salt, and the silver precipitated as chloride. As soon as the chlorine entered the solution, a white precipitate was formed, which soon changed to brown, owing to the formation of thallic hydroxide by the hydrolysis of thallic chloride. This precipitate redissolved as more chlorine was added, until finally a white precipitate of silver chloride alone remained.

It was found advisable to keep the precipitate stirred from time to time during the addition of chlorine. The liquid was then boiled to expel the excess of chlorine, and, after cooling, filtered on a Gooch crucible; the precipitate of silver chloride was washed and weighed in the usual way. The filtrate and washings were concentrated to about 150 c.c., and treated with a stream of sulphur dioxide for about ten minutes.* A few cubic centimetres of liquid sulphur dioxide can be substituted for the gas, and this has the advantage both of saving time and obviating loss of the solution by spirting. The liquid was then boiled to expel the excess of sulphur dioxide. An excess of a 20 per cent. solution of potassium iodide was then added, and the mixture boiled for about two minutes. When cold, the precipitate of thallous iodide was filtered on a Gooch crucible, washed with a 1 per cent. solution of potassium iodide until the washings were free from nitrate, and then washed with 80 per cent. alcohol, dried at 140°, and weighed. Table I gives the results of a series of analyses.

---

* The sulphur dioxide must not be added directly from the syphon, as this would occasion a violent effervescence in which there would be great danger of loss. A small quantity of the liquid is poured from the syphon into a beaker, and, from this,

Columns 1 and 2 give the weights of silver nitrate and thallous nitrate respectively contained in the solution, and 3 and 4 give the weights of silver chloride calculated and experimentally determined. Columns 5 and 6 give the calculated and experimentally determined weights of thallous iodide.

The percentage error on the silver chloride is never greater than 0·1, whilst that on the thallous iodide varies between 0·2 and 0·4:

TABLE I.

1. $AgNO_3$ taken.	2. $TlNO_3$ taken.	3. AgCl calc.	4. AgCl obtained.	5. TlI calc.	6. TlI obtained.
1·0499	0·3184	0·8856	0·8853	0·3960	0·3970
1·0006	0·1127	0·8440	0·8440	0·1401	0·1398
0·5487	0·2661	0·4628	0·4625	0·3310	0·3296
0·5317	1·3035	0·4485	0·4485	1·3082	1·3035
0·1086	0·9992	0·0917	0·0918	1·2429	1·2428

II. *Determination of the Solubility of Thallous Chloride in Potassium Carbonate.*

In a series of experiments involving the use of potassium carbonate and thallous salts, it was found that the addition of potassium chloride to a solution containing potassium carbonate and thallous salts gave, as was to be expected, a precipitate of thallous chloride. When this precipitate had been filtered off, the addition of sufficient dilute sulphuric acid to neutralise the potassium carbonate caused the precipitation of a further quantity of thallous chloride. On investigation, this was found to be due to an increased solubility of thallous chloride in potassium carbonate solution, for, whereas thallous chloride dissolves to the extent of 3·86 grams per litre in water at 25°, it is soluble to the extent of 21·84 grams per litre in a 5*N*-solution of potassium carbonate. A study of the curve representing the

the sulphur dioxide is carefully poured down the side of the vessel containing the substance to be reduced. The first few drops produce a mass of fine ice crystals on the surface of the solution which effectually prevents any loss when the residue of the liquid is added. Reduction by means of liquid sulphur dioxide is only recommended when a good draught is obtainable.

increase of solubility gives no indication of the presence of double salts.

The potassium carbonate used in these determinations was Kahlbaum's purest, but was found to contain small quantities of potassium hydroxide, and was therefore purified by digesting with alcohol.

The potassium carbonate was dissolved in water to make solutions of various strengths, which were accurately determined by titration. Dry thallous chloride was added to these solutions, placed in a series of bottles. The bottles were then closed by well-fitting stoppers, which were also covered with watertight caps, and placed in a thermostat at 25° and shaken for several days. When the solutions were saturated with thallous chloride, they were carefully analysed, the thallium being estimated by the method already described. The results of a series of determinations are given in table II. Column 1 gives the concentration of potassium carbonate in gram-molecules per litre; column 2 that of thallous chloride in gram-molecules per litre; column 3 the increase in solubility of thallous chloride in gram-molecules due to the presence of potassium carbonate:

TABLE II.

1. Conc. K_2CO_3.	2. Conc. TlCl.	3. Increased solubility of TlCl.
0·0000	0·0161	0·0000
0·0093	0·0184	0·0023
0·0186	0·0201	0·0040
0·0465	0·0239	0·0078
0·0930	0·0289	0·0128
0·4650	0·0489	0·0328
0·8887	0·0636	0·0475
1·3330	0·0744	0·0583
1·7774	0·0816	0·0655
2·2217	0·0862	0·0701
4·4435	0·0904	0·0743
5·0763	0·0915	0·0754

A curve showing the relationships between the increase in the concentration of the potassium carbonate and that of the thallous chloride gives no indication of the formation of a double salt. The general form of the curve is a hyperbola, as is evident from the figures in table II. Whether or no there are complex ions in the solution cannot be decided from solubility determinations, but would follow from a determination of the electropotential of such solutions against a thallium electrode. Determinations of this nature are in progress.

The cost of material used in this investigation was covered by portion of a grant from the Research Fund Committee of the Chemical Society.

CHEMICAL LABORATORY,
BEDFORD COLLEGE,
BAKER STREET, W.

LXXXI.—*The Constituents of Cyprus Origanum Oil. Isolation of a New Terpene (Origanene).*

By Samuel Shrowder Pickles, M.Sc.

During his visit to Cyprus, in 1904, Prof. W. R. Dunstan obtained a small quantity of the oil distilled locally from the principal origanum plant of the island, and arranged for further supplies to be forwarded to the Imperial Institute for examination. An account of the preliminary examination was published in the Bulletin of the Imperial Institute (1906, p. 296). The physical constants of the oil were recorded, and it was shown that the principal constituent of the oil is carvacrol, which is present to the extent of 82·5 per cent.

The present investigation, undertaken at the suggestion of Prof. Dunstan, deals with the further examination of the constituents of this oil.

Of several oils of origanum and thyme produced in Cyprus, this, the most important, is the origanum oil, resembling that known in commerce as "oil of Cretan origanum," about 3000 lbs. of which are now annually exported.

Oils containing carvacrol are obtained from several species of *Origanum* growing in countries bordering on the Mediterranean, the two chief being (1) Trieste origanum oil, which, according to Gildemeister and Hoffmann (*Volatile Oils*, p. 622), is probably derived from *Origanum hirtum*, Lk., and (2) Smyrna origanum oil, derived from *Origanum Smyrnaeum*, Linn. According to the Index Kewensis, the latter is a synonym for *O. Onites*, Linn.

There is at present some little doubt as to the exact botanical species of the plant furnishing the Cyprian oil. It is known in the island by the name "Ριγανη," and is regarded by Dr. Gennadius, late Director of Agriculture for Cyprus, as *Origanum Onites*. Holmboe, a Norwegian botanist, regards the plant as *O. dubium*, a sub-species of *O. Maru*, L. A botanical specimen sent recently to Kew was identified as *Origanum majorana*, although the oil differs widely from that produced by *O. majorana* as grown in Spain. Holmes (*Pharm. J.*, 1907, **79**, 378) has also recently examined the plant, and finds that, although it is closely allied to *O. majorana*, it differs from it in certain respects, particularly in being perennial, and he proposes to refer it to Willdenow's *O. majoranoides*.

The physical properties of the oil and the yield of carvacrol are almost identical with those of the Trieste oil (*O. hirtum*, Lk.). On the other hand, the low content of carvacrol in Smyrna origanum oil (from 25 to 60 per cent.) appears to indicate a different botanical origin.

Trieste origanum oil was examined by Jahns (*Arch. Pharm.*, **215**, 1) in 1879, who first showed that the oil contained carvacrol. He also obtained small quantities of another phenol (0·2 per cent.), which was not identified, but which was said to produce a violet coloration with ferric chloride. Jahns further stated that the non-phenolic portion of the oil, after several rectifications over sodium, boiled for the most part between 172° and 176°, and consisted principally of cymene, the presence of which was shown by the formation of cymenesulphonic acid. He also mentioned that this fraction, when shaken with concentrated sulphuric acid, developed the odour of sulphur dioxide, a fact which would seem to indicate the presence of terpenes.

Smyrna origanum oil was examined by Gildemeister in 1895 (*Arch. Pharm.*, **233**, 182). It was found to differ from the Trieste oil in that it contains the aliphatic alcohol, linalool, in considerable amount. On account of the low specific gravity of the hydrocarbon fraction, 155—163° (sp. gr. = 0·826), it was thought to contain olefinic terpenes. Besides carvacrol, the oil was shown to contain cymene and *l*-linalool.

An analysis of Cyprus origanum oil by Francis (*Chemist and Druggist*, 1907, **70**, 366), Government Analyst of Cyprus, has also recently been published. From the results given, however, it would seem that he had merely distilled the oil and named the various fractions on the assumption that the oil was a thyme oil, without attempting to examine them chemically. His results are as follows:

	Sample No. 1.	Sample No. 2.
Water	2·60	2·00
Light oil, boiling below 160°	1·80	2·00
Thymene, distilling at 160—165°	6·40	2·40
Cymene, ,, 170—180°	7·60	8·80
Thymol, ,, 230°	81·60	84·80
	100·00	100·00

If the above surmise is incorrect, some other explanation of these results is required, as 230° is the correct boiling point for thymol, whereas carvacrol boils at 236°. Francis also remarks that the best way to remove the thymol is to cool the oil to 0°, when the thymol separates. Now, as the melting point of pure carvacrol is 0°, it cannot be made to crystallise from an oil merely by cooling to that temperature, although thymol (m. p. 51·5°), were it present, might reasonably be expected to do so.

Further, the hydrocarbon (b. p. 160—165°) is certainly not identical with thymene (probably *l*-pinene) isolated by Lallemand (*Compt. rend.*, 1853, **37**, 498) from thyme oil.

Occurrence and Constitution of "Origanene."

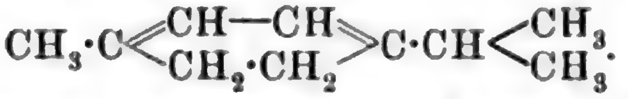
During the course of the present investigation, an examination of the hydrocarbons contained in Cyprus origanum oil revealed the presence of a terpene, the properties and derivatives of which do not coincide with those of any previously described member of the terpene group. The name "origanene" is proposed for this hydrocarbon, and it has been considered of interest to elucidate as far as possible the constitution of this apparently new substance. With this object in view, the following ascertained facts are to be considered.

Analysis shows the formula of origanene to be $C_{10}H_{16}$. Its specific gravity at 16° is 0·847, and refractive index $(n_D) = 1·480$. As obtained by distillation, the hydrocarbon has a slight optical rotation ($+1°50'$ in a 1-dcm. tube), but, as all the hydrocarbon fractions of the oil also show a slight rotation, this is possibly due to the presence, as impurity, of a small quantity of some strongly active substance. The boiling point of the terpene was found on two different occasions to be 160—164°/750 mm. and 163—166°/765 mm.

On treatment with bromine in the cold, origanene forms only a dibromo-additive compound, and by the action of hydrogen bromide in acetic acid solution, even at 130° in a sealed tube, only a monohydrobromide is obtained. By shaking origanene with dilute sulphuric acid for five days, it is partly converted into terpin hydrate. Only a slight pink coloration is produced when the hydrocarbon is dissolved in acetic anhydride and a drop of sulphuric acid is added. When origanene dibromide is treated with alcoholic potash, hydrogen bromide is readily eliminated from the molecule, and the resulting product is *p*-cymene.

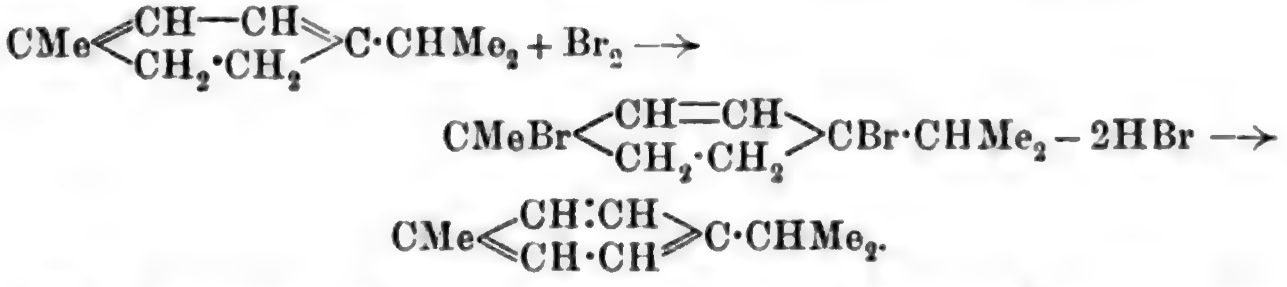
Origanene yields a colourless, crystalline *nitroso-chloride*, but apparently does not form a solid nitrosite as do the phellandrenes and terpinene. On oxidation of the hydrocarbon by hydrogen peroxide in neutral solution, succinic acid is produced.

The comparatively low boiling point of the hydrocarbon suggested the possibility of its being either an open-chain terpene of the myrcene type, or a bridged cyclic compound of the pinene or fenchene type. The high specific gravity (0·847) and the fact that only a dibromide is formed on treatment with bromine, render the open-chain theory untenable. On the other hand, the bridged cyclic terpenes, pinene, fenchene, &c., have specific gravities higher than that of origanene, and, on heating terpenes of this class with an acetic acid solution of hydrogen bromide, the bridged linking is usually resolved and dihydrobromides are formed. The other alternative is to consider origanene as a monocyclic compound containing two conjugated ethylenic linkings, and this view agrees best with the experimental evidence. The molecular refraction is found to be 45·54, which agrees with the value calculated for $C_{10}H_{16}|\!=_2$ (45·24), whereas $C_{10}H_{16}|\!=$ requires 43·53. Assuming that there is one closed ring in the molecule, the formation of terpin hydrate on shaking origanene with dilute sulphuric acid, taken in conjunction with the observations that *p*-cymene is readily formed from origanene and that on treatment with acetic anhydride and sulphuric acid only a slight pink coloration is produced, leads to the conclusion that the terpene is a *p*-menthadiene. Having regard to the ease with which origanene dibromide yields *p*-cymene on treatment with alcoholic potash, it appears probable that both the bromine atoms are in the ring, and, if so, it follows that both the double bonds must previously have been in the ring. Finally, of the possible *p*-menthadienes having a conjugated system of double bonds inside the ring, only one can give succinic acid on oxidation, namely, the $\Delta^{1:3}$-*p*-menthadiene,



$$CH_3\cdot C\Big\langle\begin{matrix}CH-CH\\CH_2\cdot CH_2\end{matrix}\Big\rangle C\cdot CH\Big\langle\begin{matrix}CH_3\\CH_3\end{matrix}.$$

Accepting this formula for origanene, the formation of the dibromide can reasonably be represented as follows:

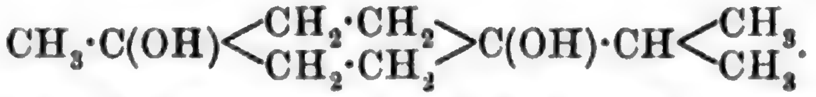


$$CMe\Big\langle\begin{matrix}CH-CH\\CH_2\cdot CH_2\end{matrix}\Big\rangle C\cdot CHMe_2 + Br_2 \longrightarrow$$

$$CMeBr\Big\langle\begin{matrix}CH{=}CH\\CH_2\cdot CH_2\end{matrix}\Big\rangle CBr\cdot CHMe_2 - 2HBr \longrightarrow$$

$$CMe\Big\langle\begin{matrix}CH{:}CH\\CH\cdot CH\end{matrix}\Big\rangle C\cdot CHMe_2.$$

The formation of terpin hydrate from a compound having this formula appears at first sight to present some difficulty, as the product which might have been expected is the terpinene terpin, m. p. 136—137°,



$$CH_3\cdot C(OH)\Big\langle\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}\Big\rangle C(OH)\cdot CH\Big\langle\begin{matrix}CH_3\\CH_3\end{matrix}.$$

Bearing in mind, however, the ease with which isomerisation takes place amongst terpenes, especially in acid solution, it is quite conceivable that the first action of the acid is to cause a shifting of the double bonds with the formation of dipentene, which would then pass into terpineol and terpin hydrate.

The $\Delta^{1:3}$-*p*-menthadiene formula has been put forward at least twice previously as representing the constitution of other terpenes. It was suggested as the formula for terpinene by Wallach in 1891, and, although the terpinene formula most generally accepted at the present time appears to be that advanced by Harries (*Ber.*, 1902, **35**, 1169), it has never been quite abandoned by Wallach.

This same formula was ascribed by Harries (*Annalen*, 1903, **328**,

322) to one of the hydrocarbons which occur in the mixture of terpenes obtained by distilling the phosphate of dihydrocarvylamine. The boiling point of this terpene was 174—176° (10° higher than that of origanene), and succinic acid was obtained on oxidation with permanganate solution. No characteristic derivatives were, however, described, and it was not stated whether the hydrocarbon formed di- or tetra-halogen additive compounds. It is thus impossible to say whether or not it resembles origanene.

Examination of Cyprus Origanum Oil.

Physical Characters.—The oil is golden-brown in colour, but rapidly darkens on exposure to air. It possesses a rather pleasant odour, somewhat resembling that of thyme oil, has a burning taste, and produces a smarting effect when applied to the skin of the face.

Specific gravity at $15^\circ/15^\circ = 0{\cdot}967$. Optical rotation in 1-dcm. tube $= +0^\circ 12'$.

The oil gives a clear solution with one or more volumes of 80 per cent. alcohol.

Chemical Examination.—The oil was subjected to a preliminary examination for the presence of free acids by shaking a portion with sodium carbonate solution. On afterwards acidifying the alkaline washings and extracting with ether, only a trace of an acid having the odour of *iso*butyric acid was obtained. Another portion of the oil was, with negative results, tested for aldehydes and ketones by shaking with a saturated solution of sodium hydrogen sulphite.

Separation of the Phenolic Portion.—Four hundred grams of the oil were shaken with 2 litres of 5 per cent. sodium hydroxide solution, and the mixture allowed to stand for about four hours. The aqueous alkaline solution was then separated from the oily layer, and an estimation of the phenols present, based on the diminution in volume which the oil had sustained, indicated a phenol content of 82·5 per cent. It was found, however, that even after this treatment some carvacrol remained dissolved in the oily portion; this was removed by a further treatment with sodium hydroxide solution, and amounted to an additional 1·5 per cent., bringing the total phenolic content up to 84 per cent. The phenols were subsequently liberated from the alkaline solution by acidifying with dilute sulphuric acid. The oil was thus separated into (*a*) phenolic portion, and (*b*) non-phenolic portion.

Identification of Carvacrol.—The aqueous alkaline extract on treatment with sulphuric acid yielded a golden-brown oil; this was washed, first with sodium carbonate solution, then with water, and afterwards distilled at atmospheric pressure. A little water first passed over, but afterwards the temperature rapidly rose to 235°, and practically the whole of the remaining liquid distilled at 235—237°. The boiling point of pure carvacrol is 236°, whereas that of thymol is 230°. Analysis of the oil (b. p. 235—237°) yielded the following results:

0·1747 gave 0·5105 CO_2 and 0·1442 H_2O. C = 79·9; H = 9·2.
$C_{10}H_{14}O$ requires C = 80·0; H = 9·3 per cent.

The specific gravity at 15°/15° was found to be 0·9810. On dissolving a little of the oil in alcohol and adding a drop of ferric chloride solution, the green coloration characteristic of carvacrol was observed. The nitroso-derivative was prepared by treating a solution of the phenol in alcohol (previously saturated in the cold with hydrogen chloride) with a concentrated aqueous solution of sodium nitrite (Klages, *Ber.*, 1899, **32**, 1578). The yellow, crystalline compound obtained melted at 153—154°, and was identical with nitrosocarvacrol (Wallach, *Ber.*, 1892, **25**, 1663). The nitroso-compound of thymol melts at 161—162°. The phenylcarbamic ester was also prepared by the action of phenyl cyanate on the phenol in the presence of a little aluminium chloride (Goldschmidt, *Ber.*, 1893, **26**, 2086). It crystallised from dilute methyl alcohol in colourless, needle-shaped crystals, melting at 140°, and identical with those obtained from pure carvacrol.

There can, therefore, be no doubt that the phenolic portion of the oil consists almost entirely of carvacrol. Indications were, however, observed of the presence of a small quantity of another phenol. If the alkaline solution, containing the sodium salt of carvacrol, is shaken with ether, all the carvacrol can be extracted. When no more phenol is yielded to the ether, it is possible, by acidifying the aqueous liquid, to obtain a small quantity of another phenol, which differs from carvacrol in that, in alcoholic solution, it gives a beautiful purple coloration with ferric chloride. It possesses a pleasant odour similar to that of wood creosote, and is a brown, viscous liquid having a tendency to solidify:

0·1320 gave 0·3580 CO_2 and 0·1020 H_2O. C = 73·9; H = 8·6.
$C_{11}H_{16}O_2$ requires C = 73·3; H = 8·9 per cent.

Its properties are consistent with the idea that it is possibly a hydroxymethoxycymene, but the small quantity obtained (0·4 gram) did not allow of further confirmation.

Examination of the Non-phenolic Portion.—As the odour of the original oil is markedly different from that of pure carvacrol, it was considered of importance to examine more closely the non-phenolic portion of the oil. The yield, however, is only about 16 per cent. of the total, so that it was necessary to work up a fairly large quantity of the oil, the phenolic portion being removed by the process already described. The oil remaining was then subjected to distillation under reduced pressure, and thus roughly separated into three fractions. The first fraction, boiling below 80°/15 mm., was distilled from a water-bath, and afterwards a metal-bath was used. The three fractions were:

(1) Fraction boiling below 80°/15 mm.
(2) " " at 80—125°/15 mm.
(3) " " above 125°/15 mm.

These were examined separately. The first was dextrorotatory and consisted almost entirely of hydrocarbons; its examination forms the chief part of the present communication. The second portion also contained some hydrocarbons, which on redistillation boiled below 80°/15 mm., but consisted principally of a lævorotatory terpineol-like compound; the third fraction contained high boiling oxygenated compounds, which have not yet been fully investigated.

Fraction boiling below 80°/15 mm.—On redistillation, this portion was first separated into two fractions, boiling respectively at 65—69°/15—20 mm. and 69—80°/15—20 mm. The first of these distillates was further fractionated at atmospheric pressure (750 mm.), and a portion boiling fairly constantly at 160—164°/750 mm. was finally obtained. On analysis:

0·1880 gave 0·6060 CO_2 and 0·1950 H_2O. C = 87·9; H = 11·5.
$C_{10}H_{16}$ requires C = 88·2; H = 11·8 per cent.

As it was apparently not quite free from oxygen, the liquid was redistilled over sodium and analysed at once. The numbers then obtained were found to agree well with the formula $C_{10}H_{16}$:

0·1590 gave 0·5150 CO_2 and 0·1665 H_2O. C = 88·3; H = 11·6.
$C_{10}H_{16}$ requires C = 88·2; H = 11·8 per cent.

This liquid appears to consist of a hydrocarbon in a fairly pure state. Pending further investigation of its constitution, the name "*origanene*" is proposed for it. This hydrocarbon is a colourless, refractive liquid of sp. gr. 0·847 at 16°. It possesses a characteristic odour, somewhat lemon-like, but quite distinct from the odour of cymene or limonene. As obtained by distillation, it had a slight optical activity, giving a rotation of + 1°50′ in a 1-dcm. tube. A determination of the refractive index gave $n_D = 1·480$.

Derivatives of Origanene.

Nitroso-chloride, $C_{10}H_{16}$,NOCl.—For the preparation of the nitroso-chloride, the hydrocarbon (3 c.c.) was dissolved in methyl alcohol and a few drops of acetic acid were added. Amyl nitrite (4 c.c.) was then added, and, after cooling to − 10° in a freezing mixture, hydrochloric acid (2 c.c.) was dropped in gradually, the liquid being constantly shaken. The nitroso-chloride separated at once in colourless, needle-shaped crystals. More methyl alcohol was now added, and, after allowing the flask to remain in the freezing mixture for twenty minutes, the crystals were collected, well washed with methyl alcohol, and dried on a porous plate.

The *nitroso-chloride* is not a very stable compound, it decomposes at once on heating in alcoholic solution, and on standing alone for a few days becomes coloured. Its melting point, which is also a decomposition point, lies between 91° and 94°, depending on the speed of heating. At this point it decomposes violently, leaving a dark red liquid in the tube. Owing to this liability to decompose, it is difficult to obtain the compound sufficiently pure for analysis :

0·1600 gave 0·1060 AgCl. Cl = 16·4.

$C_{10}H_{16}ONCl$ requires Cl = 17·6 per cent.

The *nitrolbenzylamine*, $C_{10}H_{15}(:NOH)\cdot NH\cdot C_7H_7$.—This is formed when the nitroso-chloride is dissolved or suspended in ethyl alcohol and a slight excess of benzylamine is added. The reaction takes place almost at once, but it is advisable to warm the mixture in the water-bath and allow it to stand for a short time. On adding water, the crystalline *nitrolbenzylamine* is precipitated in small, well-defined prisms. After recrystallising from dilute methyl alcohol, the melting point was 104—105°:

0·1820 gave 0·4980 CO_2 and 0·1480 H_2O. C = 74·63 ; H = 9·0.

$C_{17}H_{24}ON_2$ requires C = 75·0 ; H = 8·8 per cent.

The *nitrolpiperidide*, $C_{10}H_{15}(:NOH)\cdot N:C_5H_{10}$, was obtained in the same way from the nitroso-chloride by using piperidine in place of benzylamine. It crystallises from methyl alcohol, ethyl alcohol, or ethyl acetate in long, colourless, prismatic needles melting at 198°:

0·2360 gave 23·0 c.c. of nitrogen at 779 mm. and 18°. N = 11·5.

$C_{15}H_{26}ON_2$ requires N = 11·2 per cent.

The *hydrochloride*.—The hydrocarbon forms only a monohydrohalide compound. For the preparation of the hydrochloride, the terpene (3 grams) was mixed with glacial acetic acid, and, after cooling in a freezing mixture, dry hydrogen chloride was passed into the solution for thirty minutes. The liquid, which had then become slightly pink, was allowed to stand for an hour, water was then added, and the mixture well shaken, when an oily liquid separated ; this was washed with more water, then with very dilute sodium carbonate solution, and dried over calcium chloride :

0·3730 gave 0·3050 AgCl. Cl = 20·24.

$C_{10}H_{17}Cl$ requires Cl = 20·58 per cent.

The *hydrochloride* is a colourless oil with a pleasant odour. Its specific gravity at 18° is 0·992.

The *dibromide.*—For the preparation of the dibromide, origanene (2 c.c.) was mixed with chloroform (4 c.c.) and cooled in a freezing mixture. Bromine in chloroform solution (1 c.c. = 1 gram Br) was then added drop by drop until the brown colour of the liquid was permanent. At this point hydrogen bromide began to be evolved. Two c.c. of the bromine solution had been added, equivalent to 2 grams of bromine. On calculation this was found to be almost exactly the quantity of bromine required for the formation of the dibromide $C_{10}H_{16}Br_2$. A current of dry air was then passed through the solution to remove the chloroform, and the liquid remaining was left in a vacuum desiccator for a short time.

The *dibromide* obtained in this way was an oily, deep yellow liquid having an odour resembling that of turpentine. It is apparently not very stable, for on standing in the open air it becomes dark coloured.

Attempts to obtain a crystalline nitrosite of origanene, such as is formed in the case of the phellandrenes and terpinene, were unsuccessful.

The *hydrobromide.*—With the object of obtaining if possible a dihydrohalide derivative of origanene, the hydrocarbon was submitted to the action of hydrogen bromide under conditions which might be expected to cause the rupture of a bridged ring, if such were present in the molecule. To the terpene (2 c.c.) a considerable excess of an acetic acid solution of hydrogen bromide (saturated at 0°) was added.

The mixture was allowed to remain in the cold for a day, and it was afterwards heated in a sealed tube to 130° for two hours. Even in these circumstances, however, only 1 molecule of hydrogen bromide could be made to combine with the $C_{10}H_{16}$ molecule. After washing the product free from acids and drying over calcium chloride, it was obtained as a yellow, oily liquid, somewhat denser than water:

0·2800 gave 0·2440 AgBr. Br = 37·1.

$C_{10}H_{17}Br$ requires Br = 36·9 per cent.

Treatment of Origanene with Dilute Sulphuric Acid. Production of Terpin Hydrate.

The hydrocarbon (5 c.c.) was mixed with a 5 per cent. aqueous solution of sulphuric acid (750 c.c.), and shaken at intervals for several days. On opening the bottle, the original odour of the terpene had disappeared, and the contents had acquired a somewhat cineol-like odour. A quantity of oil remained undissolved, and this was first separated; the aqueous solution was then saturated with ammonium sulphate, and extracted several times with ether. After the evaporation of the ethereal solution, a residue remained which became solid on cooling. On recrystallisation, the greater part separated in colourless, prismatic crystals, which melted at 118—119° and gave off water at this point. This substance was found to be terpin hydrate, and on treatment with concentrated hydriodic acid the characteristic dipentene dihydriodide, m. p. 79—80°, was produced.

From the mother liquor of the crystallisation, another set of crystals was obtained, evidently a mixture, and by treating this with ether and rapidly pouring off the solvent a partial separation was effected. This solution yielded a small quantity of crystalline material melting indefinitely between 126° and 131° without evolution of water. The quantity obtained was too small for characterisation.

Action of Alcoholic Potash on Origanene Dibromide. Production of p-*Cymene.*

For this experiment, the dibromide was prepared by dissolving the hydrocarbon in acetic acid, and, after cooling in a freezing mixture, adding bromine (in acetic acid solution) slowly until the brown colour was permanent. The acetic acid was then removed by washing with water, and the dibromide thus obtained was a pale yellow, heavy oil.

The liquid dibromide (12 c.c.) was placed in a flask, fitted with a condenser tube, together with a considerable excess of alcoholic potash, and heated on the water-bath for an hour. Potassium bromide separated almost immediately, and during the boiling the liquid became dark brown. On removing from the water-bath, much water was added, and the oily portion, which separated on standing, was run off and dissolved in ether. The solution was washed, dried, the ether evaporated, and the remaining oil was distilled in steam. The first portion to pass over was a colourless oil, lighter than water, having the odour of cymene. This constituted about 50 per cent. of the oil, and passed over in the first few minutes of the distillation. A quantity of dark-coloured, heavy oil remained in the flask, and this distilled much more slowly.

The light oil was redistilled, and was found to boil almost entirely between 173° and 176°. On adding a few drops of bromine in acetic acid to a portion of the liquid, it acquired at once a permanent brown colour, indicating a saturated condition. On analysis:

0·1250 gave 0·1190 H_2O. $H = 10·5$.
0·1665 „ 0·1600 H_2O. $H = 10·6$.

$C_{10}H_{14}$ requires 10·45 per cent.

The hydrocarbon was dissolved in concentrated sulphuric acid and heated on the water-bath at 90° for a few minutes, the product was poured into water, neutralised with barium hydroxide, and the mixture then heated to boiling and filtered while hot. The aqueous filtrate was evaporated, and the residue obtained, after recrystallising from alcohol, consisted of the shining, leafy crystals characteristic of the barium salt of *p*-cymenesulphonic acid. This salt has the composition $(C_{10}H_{13}O_3S)_2Ba,3H_2O$. It was heated in the air-oven at 110° until anhydrous, and then analysed:

0·3030 gave 0·1260 $BaSO_4$. Ba = 24·4.

$C_{20}H_{26}O_6S_2Ba$ requires Ba = 24·3 per cent.

Finally, the cymenesulphonic acid was obtained by decomposing the barium salt with sulphuric acid; it separated from dilute sulphuric acid, on evaporation, in plate-like crystals, melting at 50—51° and having the composition $C_{10}H_{13}\cdot SO_3H,2H_2O$.

Oxidation of Origanene with Hydrogen Peroxide. Production of Succinic Acid.

The terpene (5 c.c.) was mixed with a 33 per cent. solution of hydrogen peroxide quite free from acid (the "perhydrol" of Merck), and the mixture was shaken for some time in the cold and afterwards during heating on the water-bath. After about one hour, the solution, which had become acid, was neutralised with potassium hydroxide and allowed to stand overnight. The contents of the flask were then found to have again become acid, and, after further neutralisation, the aqueous layer was separated and evaporated to a small bulk. The liquid was then acidified, and a current of steam was passed through to remove the volatile acids. The remaining portion was again evaporated almost to dryness, and extracted several times with ether. This ethereal solution, on evaporation, yielded an oil which soon deposited crystals, and, after standing for two days, the crystalline portion was dried on a porous plate and recrystallised from water. It then melted at 184—185°, and possessed the crystalline form and characteristic bitter taste of succinic acid. On mixing a little with pure succinic acid, the melting point was not altered. A small quantity of the acid was heated in a test-tube with a large excess of acetic anhydride for ten minutes. Most of the acetic anhydride was then evaporated, and the remaining liquid was allowed to remain over potash in a vacuum desiccator for a day. The residue was then found to consist of needle-shaped crystals melting, without further purification, at 119°. The melting point of succinic anhydride is 119—120°. On adding a few drops of water and heating to dryness on the water-bath, succinic acid, m. p. 184—185°, was again formed.

Previous to the employment of hydrogen peroxide as the oxidising agent, nitric acid and potassium permanganate had been tried, but the oxidation products obtained did not provide the conclusive evidence required. The nitric acid oxidation yielded oxalic acid and a nitrated product which could not easily be identified. Permanganate solution, on the other hand, gave oxalic, acetic, and *iso*butyric acids, and an uncrystallisable syrup.

Examination of Fraction Boiling at 60—80°/15—20 *mm.*

Identification of Cymene.—This fraction had a distinct odour of cymene, and, as this hydrocarbon had been previously recognised as a constituent of origanum oil, it was hoped that a separation would be possible simply by distillation. On analysing the various distillation products, however, the results obtained always indicated a mixture of compounds of the formulæ $C_{10}H_{14}$ and $C_{10}H_{16}$. Moreover, the different fractions rapidly decolorised permanganate solution, and combined immediately with bromine even in the cold. The following is a typical analysis of the fraction boiling at 174—175°:

0·1310 gave 0·4260 CO_2 and 0·1300 H_2O. C = 88·7; H = 11·02.

$C_{10}H_{14}$ requires C = 89·5; H = 10·5.

$C_{10}H_{16}$ „ C = 88·2; H = 11·8 per cent.

A mixture containing equal parts of $C_{10}H_{14}$ and $C_{10}H_{16}$ would require C = 88·8, H = 11·2 per cent., which is very near the result actually obtained.

Oxidation to p-*Hydroxy*iso*propylbenzoic Acid.*—For the identification of cymene, 2 grams of the above fraction were oxidised with potassium permanganate solution (12 grams in 330 c.c. of water) by heating the mixture on the water-bath until the colour of the permanganate had disappeared. The manganese dioxide was then removed, and the aqueous solution evaporated to dryness. The potassium salts remaining were boiled with alcohol, which dissolves the salt of *p*-hydroxy*iso*propylbenzoic acid, the solution filtered, evaporated to dryness, and the acid liberated with dilute sulphuric acid. In this way, *p*-hydroxy*iso*propylbenzoic acid was obtained, which, after recrystallising from alcohol, melted at 156—157°.

On boiling a portion of this acid for a few minutes with fairly concentrated hydrochloric acid, it was converted into *iso*propenylbenzoic acid. This was dried on a porous plate, crystallised from diluted ethyl alcohol, and was then found to melt, after previous darkening, at 256—257°.

As it is conceivable, however, that cymene might be produced from certain terpenes by oxidation, an attempt was made to isolate cymene by another process. The fraction boiling at 174—176° was mixed with glacial acetic acid and cooled in a freezing mixture. Dry hydrogen chloride was then passed through the liquid until it was saturated, the terpenes present being thus converted into the hydrochlorides. After removing the free acids by washing several times with water, the remaining liquid was carefully heated in a distilling flask under a pressure of 13 mm. A distillate was obtained which boiled between 70° and 80°/13 mm.; this was redistilled, and the lowest boiling fraction collected separately. This had the characteristic odour of cymene, and on analysis gave figures agreeing approximately with the formula $C_{10}H_{14}$. On oxidation, this also gave *p*-hydroxy*iso*propylbenzoic acid (m. p. 155—156°) as in the former case.

Presence of a Third Hydrocarbon.—It has been observed that it was found impossible, by distillation, to separate the cymene from a terpene fraction boiling about the same temperature. As this is from 10° to 15° higher than the boiling point of origanene, the presence of a third hydrocarbon was suspected. The suspicion was confirmed on examining the product obtained by treating the cymene fraction with hydrochloric acid, for it was found that a considerable quantity of a dihydrochloride ($C_{10}H_{16}$,2HCl) had been formed. It has been shown that origanene forms only a monohydrochloride under the same conditions. Owing to the difficulty in separation, however, this third hydrocarbon has not been identified. It yields only oily halogen and hydrogen halide derivatives, and, although a striking blue colour is produced with amyl nitrite and hydrochloric acid, no solid nitroso-chloride separates out. It is readily attacked in the cold by Beckmann's chromic acid mixture, and is therefore possibly a compound of the terpinene type.

Fraction Boiling at 80—125°/10—15 mm.

On redistilling this fraction, a considerable quantity of a liquid boiling below 80° was first obtained. This consisted mainly of hydrocarbons, and was added to the previous fraction. The remainder boiled for the most part at 110—120°/10—15 mm. It possessed a pleasant odour, reminiscent of menthol and camphor, and on cooling in a freezing mixture it became very viscous, but could not be made to solidify. The specific gravity at 14° was 0·934.

The fraction was slightly lævorotatory, giving a rotation of – 4°0 in a 1-dcm. tube:

0·1600 gave 0·4600 CO_2 and 0·1640 H_2O. C = 78·4; H = 11·4.

$C_{10}H_{18}O$ requires C = 77·9; H = 11·7 per cent.

The somewhat camphor-like odour suggested the possible presence of a ketone, but attempts to obtain a semicarbazone, phenylhydrazone, or oxime were unsuccessful. Previous to the analysis, the oil had been treated with alcoholic potash to test for the presence of esters, but a subsequent examination of the potash solution failed to reveal the presence of acids.

Action of Phenyl Cyanate.—A small quantity of this fraction (2 c.c.) was mixed with an equal volume of phenyl cyanate and allowed to stand, without heating, for two weeks. A slight pink colour had developed, and a crystalline solid had then separated, but the bulk of the mixture remained liquid even after a subsequent heating on the water-bath. The solid which had separated was found to be diphenylcarbamide (m. p. 235°), produced by the phenyl cyanate abstracting the elements of water from the compound. No phenylcarbamic ester was formed.

Treatment with Phthalic Anhydride.—With the view of obtaining a phthalic acid ester of the compound, 2 c.c. of the above fraction were mixed with phthalic anhydride and a little benzene, and heated on the water-bath for two hours; the combination which had taken place was, however, almost negligible, as on treating the contents of the flask with cold sodium hydroxide solution, and afterwards titrating with sulphuric acid, almost all the phthalic anhydride was found to be present as phthalic acid.

Action of Dilute Sulphuric Acid. Conversion into Terpin Hydrate.—A portion of the same fraction (5 c.c.) was mixed with benzene (2·5 c.c.) and shaken with 750 c.c. of 5 per cent. sulphuric acid for five days. At the end of this time, the oily liquid, consisting of benzene and a little of the original liquid which had remained unchanged, was separated, and the acid aqueous portion was then saturated with ammonium sulphate and extracted several times with ether. The ethereal extract was evaporated to a small bulk and allowed to cool. Prismatic crystals soon separated, which melted at 117—118°. They were identical in crystalline form with terpin hydrate, and on mixing the two together no lowering in melting point was observed.

A quantity of this crystalline material was shaken for a few minutes with concentrated hydriodic acid (sp. gr. 1·94). A solid compound was at once formed, which after recrystallisation from light petroleum melted at 79—80°, the correct melting point of dipentene dihydriodide.

The original oil (fraction 110—120°/10—15 mm.) on treatment with hydriodic acid does not yield a solid dihydriodide. This fraction would thus seem to consist of a terpene alcohol similar to, although not identical with, terpineol.

Portion Boiling above 125°/10—15 mm.

The higher boiling fraction (above 125°/10—15 mm.) is a viscous, highly-coloured liquid, the odour of which is quite different from that of the preceding fraction. It is apparently a mixture of oxygenated compounds, but up to the present no single substance has been obtained from it in a condition sufficiently pure for characterisation.

It contains no methoxy- or ethoxy-compounds, and esters, if present at all, form only a very small proportion of this fraction.

Summary of Constituents.

The constituents of the origanum oil of Cyprus may be summarised as follows:

(1) Carvacrol, about	84·0 per cent.
(2) A second phenol having a creosote-like odour, about...	0·2 ,,
(3) Free acid, probably *iso*butyric acid	trace
(4) Origanene, $C_{10}H_{16}$, about	2·5 ,,
(5) Cymene (6) Terpenes } b. p. 170—180°, about	8·5 ,,
(7) Terpene alcohols (b. p. 100—125°/10—15 mm.), about	3·5 ,,
(8) Residue, boiling above 125°/10—15 mm., about..	1·3 ,,

In conclusion, the author wishes to acknowledge his indebtedness to Prof. W. R. Dunstan, Director of the Imperial Institute, in whose laboratory the investigation has been conducted, and also to Mr. B. J. Eaton, who made some of the original estimations and experiments on Cyprus origanum oil.

IMPERIAL INSTITUTE,
SOUTH KENSINGTON, S.W

LXXXII.—*The Molecular Complexity of Amides in Various Solvents.*

By ANDREW NORMAN MELDRUM and WILLIAM ERNEST STEPHEN TURNER.

THE theory of solution recognises that a solute may exist in three distinct conditions, namely, (1) in single molecules (the normal condition), (2) in the ionised state, and (3) in associations of molecules. Numerous instances of each of these came under the notice of Raoult (*Ann. Chim. Phys.*, 1884, [vi], **2**, 66), but could not be rightly distinguished from one another until 1887, when the van't Hoff-Avogadro hypothesis indicated which should be regarded as the normal state of things. It was then found that the phenomenon of association in solution was of common occurrence.

As to the cause of the phenomena of dissociation and association, the theory of electricity indicates that there exists a close connexion between the dielectric constant of a solvent and the extent to which it allows of dissociation or association of the solute. This was first indicated by J. J. Thomson in a paper on the discharge of electricity through gases. He points out that "if the forces which hold the molecule together are electrical in their origin, ... these forces will be very much diminished when the molecule . . . is surrounded by a substance like water possessing a very large specific inductive capacity" (*Phil. Mag.*, 1893, [v], **36**, 313). So much for electrolytic dissociation. On the other hand, it is obvious that in the case of a solute the molecules of which tend to associate, this tendency may have free play in a solvent of low specific inductive capacity, and may be hindered by a solvent the specific inductive capacity of which is high. This corollary to Thomson's proposition is due to Nernst, who says, "Wir werden erwarten können, dass Lösungsmittel um so stärker Doppelmolecüle zu spalten vermögen, d.h. eine um so grössere dissocierende Kraft besitzen, je grösser ihre D. E. ist. Dies bestätigt sich vollkommen. . . ." (*Zeitsch. physikal. Chem.*, 1894, **13**, 535).

The early work of Raoult was variously corrected and confirmed and extended by Beckmann (*Ber.*, 1888, **21**, 766, 1163; *Zeitsch. physikal. Chem.*, 1888, **2**, 715) and Paternò (*Ber.*, 1888, **21**, 3178; 1889, **22**, 1430; *Gazzetta*, 1889, **19**, 640). This work is usually summarised in the statement that phenols, alcohols, carboxylic acids, and oximes, that is, hydroxylic substances, are associated in benzene solution.*

Much of the subsequent work in the field of molecular association in solution has been done under the direction of Auwers. In the course of this work, observations on acetanilide and certain urethanes having shown that these substances are associated in benzene solution (Auwers and Ewing, *Zeitsch. physikal. Chem.*, 1893, **12**, 689), a special study of the amides was made by Auwers in conjunction with Phul (*loc. cit.*, 1894, **15**, 33), Pelzer (*loc. cit.*, 1897, **23**, 449) and Dohrn (*loc. cit.*, 1899, **30**, 529). The phenols had been shown to possess a strong tendency to association in hydrocarbon solution, and now the amides were found to be cryoscopically abnormal in even a higher degree than the phenols.

This resemblance between the phenols and the amides leads naturally to a consideration of their chemical constitution. The tendency of the alcohols and phenols to molecular association being ascribed to the presence in these substances of the hydroxyl group, one must doubtless ascribe the same tendency in the amides to the hydroxyl group again. So Auwers reasoned in 1893.

The conjecture that the amides by constitution are hydroxylic compounds, moreover, fell in with the tendencies of organic chemistry. So long ago as 1868, Wanklyn and Gamgee (*Journ. Chem. Soc.*, **21**, 31) had said in advocating for carbamide the constitutional formula $NH{:}C(NH_2){\cdot}OH$, "this formula is not new." For thiocarbamide,

---

* As a matter of fact, numerous exceptions to this statement are to be found in Paternò's work.

Rathke (*Ber.*, 1881, **14**, 1776) was the first to suggest the formula $NH{:}C(NH_2){\cdot}SH$. In 1890, Tafel and Enoch (*Ber.*, **23**, 103) suggested that benzamide has the constitution $NH{:}CPh{\cdot}OH$ and not $NH_2{\cdot}COPh$, because of the ease with which they were able to obtain from it Pinner's benziminoethyl ether, $NH{:}CPh{\cdot}OEt$.

In Auwers' series of researches, the solvent was always a hydrocarbon. Beginning with the observation that benzamide is associated when dissolved in water, we have studied the molecular complexity of the amides in a variety of solvents. In this way, we have obtained much information that we did not expect, and could not have obtained had we confined our work to one class of solvent.

On beginning this work, we had to decide which of the several molecular weight methods to adopt, and then which of the various forms of apparatus to use. The freezing-point method, which admittedly gives more accurate values than the boiling-point method, would have meant a far too restricted choice of solvents and of amides for our purposes. Auwers, who used the freezing-point method, confined himself to one solvent throughout a research. In the earlier researches, benzene was used, but this was abandoned later in favour of naphthalene, so as to avoid the poor solvent power of benzene at its freezing point. We decided to use the boiling-point method, and were thereby enabled to include ethyl alcohol among the solvents studied, and among the amides many which are sparingly soluble in water at 0°. As it turned out, these are two important advantages.

For a preliminary survey of the field, we used the modification of Landsberger's apparatus introduced by Walker and Lumsden (Trans., 1898, **73**, 502). We next used the Beckmann apparatus; in this case the process is slow, a disadvantage in itself, and one which leads to other disadvantages. There may be a loss of solvent by diffusion of vapour, and when the solvent is water there are special difficulties. The tendency to superheating is greater than with any other solvent, and the elevation of boiling point smaller, so that the effect of superheating is more dangerous. Further, in the course of a protracted experiment, alkali may be dissolved from the glass vessel, and hydrolysis of the amide may go on.

The Lumsden-Walker process has the cardinal virtue of being expeditious, so that it almost avoids the difficulties which beset the Beckmann process. Moreover, as the work advanced, we found that the apparatus could be used for the purpose of more accurate work than the devisers of it had believed. They say, expressly, that their method is adapted for obtaining values easily and rapidly in the course of ordinary organic and inorganic research work, but not for obtaining accurate values for physico-chemical purposes (*loc. cit.*, p. 503).

The possible sources of error in the Lumsden-Walker method are three: (1) The process may be regarded as consisting of the distillation of a liquid. Fractionation goes on, so that if the liquid is impure, for this reason alone the boiling point rises, an error which we avoided, so far as our experiments required, by careful purification of the solvent.

(2) Usually, the amount of the solvent is determined by weighing. In the Lumsden-Walker apparatus the volume of the solution is measured, and taken to be proportional to the solvent. This procedure, which is due in principle to Arrhenius (*Zeitsch. physikal. Chem.*, 1888, **2**, 493), and which has been followed recently by Price (Trans., 1907, **91**, 531) and by Blackman (Proc., 1906, **22**, 175; *J. Physical Chem.*, 1907, **11**, 681), involves the assumption that the volume change which accompanies the process of solution is negligible. Expansion during solution, which as a matter of fact often occurs, means that the quantity of solvent is somewhat overestimated by the volume method, and this again means that the molecular weight of the solute is found too low. A comparison between the two methods instituted by Beckmann (*Zeitsch. physikal. Chem.*, 1881, **2**, 736) showed that they do not lead to quite the same result, the volume method giving lower results than the other, especially at higher concentrations of the solution, and such is our experience, also, in carrying out experiments by the two methods side by side.

It is by no means certain, according to the ordinary solution theory, that the results of the weight method are right, and those of the volume method wrong. Beckmann was careful not to decide between the two (*loc. cit.*, p. 740). Expansion during solution has a consequence besides the one already mentioned. It involves a diminution of the concentration of the solution, and at the same time presumably a diminution both of the osmotic pressure and of the boiling-point elevation. Finally, if the elevation of the boiling point is too small, the molecular weight is found too large, and this error has free play in the weight method, whilst in the volume method it is compensated for, more or less, by the other error, which is in the opposite direction.

Morse and Frazer (*Amer. Chem. J.*, 1905, **34**, 1) have measured the osmotic pressure of solutions of sucrose in water, and in that connexion have specially considered the effect of volume changes. They say (*loc. cit.*, p. 92), "cane sugar in solution exerts an osmotic pressure throughout the larger volume of the solution equal to that which, as a gas, it would exert if confined to the smaller volume of the pure solvent." If this view, which involves a considerable modification of the ordinary solution theory, is true for solutions in general, then the weight method is undoubtedly superior to the other.

Actually, there is not much difference between the molecular weights furnished by the two methods when the solutions are dilute, and this condition is fulfilled wherever in our paper we compare the extent of association of different amides. Further, from Lumsden's results (Trans., 1907, **91**, 32), it would appear that the molecular volume of a particular substance in different solvents does not vary enough to be appreciable in molecular-weight determinations.

(3) The main source of error was pointed out by Walker and Lumsden. When the volume of liquid in the vessel is great, the pressure at the bottom of the vessel is greater than when the volume is small, and consequently the observed boiling point is higher in the first case than in the second, and this even when the solvent alone is present. So great is the effect in the case of carbon disulphide, they say, as to preclude the use of that solvent.

We therefore determined by experiment the elevation of boiling point of each of our solvents corresponding with a certain increase in the column of liquid, and the data thus obtained * have been used throughout this paper so as to correct the boiling points of solutions for the error in question.

Although in this work we have used the Lumsden-Walker apparatus, and that in its original form,† we have carried out some comparative experiments, in which the volume and the weight of the solution were measured. The boiling tube, corked to prevent evaporation of the solvent, need be weighed only to the nearest centigram, and the special correction introduced by us (together with a correction for any variation in the barometer) allows of what Landsberger did not attempt, namely, a series of readings at different dilutions. The process is speedy, and we believe that it avoids the disadvantages of the Beckmann process without loss of accuracy.

The Beckmann thermometer is somewhat inconvenient for use in the Lumsden-Walker apparatus, because it occupies too much space in the boiling tube, and causes excessive frothing of the liquid. We used the Landsberger set of thermometers, the scales of which are divided into 0·05°, and can be read to 0·005°.

---

* The data were obtained by experiments with the solvents only, and not with the solutions. The thermometer and delivery tube were removed before the height of the liquid column was read, so that the correction per centimetre of liquid is obviously different when a thermometer, or a delivery tube, or a boiling tube of different diameter from ours is used. In this paper, we quote the data chiefly as an indication of the amount of the error in question:

Solvent.	Elevation of b. p. per 2 mm. of liquid.	Solvent.	Elevation of b. p. per 2 mm. of liquid.
Alcohol	0·0027	Ether	0·0032
Benzene	0·0035	Acetone	0·0037
Chloroform	0·0064	Water	0·0044

† Numerous modifications of the original apparatus have been introduced, not all of them improvements.

EXPERIMENTAL.

Materials.—The acetamide (m. p. 79—80°),* benzamide, salicylamide (m. p. 138°), and benzanilide (m. p. 160°) were obtained from Kahlbaum, the carbamide (m. p. 132°) from Schuchardt, and the trichlorolactamide from Merck. Monochloroacetamide (m. p. 119°), dichloroacetamide (m. p. 99·5°, usually given as 96° or 98°), trichloroacetamide (m. p. 140°), and malonamide (m. p. 168°) were prepared by us from ammonia and the corresponding ester.

The benzamide was crystallised twice from water and once from benzene. Two specimens from Kahlbaum and two specimens prepared by us melted at 126° and not 128°, the melting point usually given.

The alcohol, acetone, benzene, chloroform, and ether were fairly pure. Each solvent was dried very carefully and then fractionated, using the Young pear still-head. In the case of a number of fractions, the boiling point was constant within 0·005°. No fraction was used of which the boiling-point range was more than 0·02°, except in the case of two small samples of chloroform, where the range was 0·03°, and these were used for experiments in which the elevation of boiling point was large.

The following solvent constants are calculated from the weight-constants given by Beckmann, Fuchs, and Gerhardt (*Zeitsch. physikal. Chem.*, 1895, **18**, 473), and the specific gravities of the solvents at the boiling points given by Beckmann (*Zeitsch. physikal. Chem.*, 1890, **6**, 412):

Alcohol	1590	Ether	3100
Benzene	3200	Acetone	2270
Chloroform	2550	Water	530

In the following tables V denotes volume of solution in c.c.

Δ „ elevation of boiling point (corrected).

N „ number of milligram molecules of solute per 100 c.c. of solution.

M „ molecular weight in solution.

M is calculated from the equation

$$M = \frac{\text{volume constant} \times \text{weight of solute}}{V \times \Delta}.$$

---

* The melting points were all determined in the same way, with the thermometer bulb at the centre of a long-necked glass bulb containing sulphuric acid.

Solvent—Benzene.

Benzamide (M.W. = 121), 0·716 gram.

V.	Δ.	N.	M.
21·4	0·590	27·6	181
31·4	0·440	18·8	166
37·7	0·375	15·7	162
48·6	0·300	12·2	157

Acetanilide (M.W. = 135), 2·232 grams.

V.	Δ.	N.	M.
32·4	0·930	51·0	237
35·9	0·865	46·0	230
39·65	0·815	41·7	221
44·2	0·745	37·4	217

Monochloroacetamide (M.W. = 93·5), 0·322 gram.

V.	Δ.	N.	M.
23·0	0·350	15·0	128
28·4	0·280	12·1	130
35·4	0 220	9·7	132

Trichloroacetamide (M.W. = 162·5), 2·930 grams.

V.	Δ.	N.	M.
29·4	1·415	61·3	225
33·1	1·265	54·4	224
36·8	1·165	49·0	219
40·7	1·060	44·3	217

Salicylamide (M.W. = 137), 1·100 grams.

V.	Δ.	N.	M.
35·0	0·560	23·0	180

0·685 gram.

V.	Δ.	N.	M.
23·95	0·525	21·6	174
30·4	0·420	16·5	172
35·4	0·380	14·1	163
43·4	0·315	11·5	160

Benzanilide (M.W. = 197), 0·762 gram.

V.	Δ.	N.	M.
19·3	0·570	20·0	222
26·6	0·420	14·5	218
34·4	0·330	11·2	215

Dichloroacetamide (M.W. = 128), 1·550 grams.

V.	Δ.	N.	M.
28·9	0·915	41·9	187
32·8	0·835	36·9	181
36·2	0·765	33·4	179
41·0	0·680	29·5	178

Trichlorolactamide (M.W. = 192·5), 1·190 grams.

V.	Δ.	N.	M.
23·4	0·570	26·4	286
28·0	0·490	22·1	277
33·6	0·430	18·4	264
42·0	0·360	14·7	252

Solvent—Chloroform.

Benzamide (M.W. = 121), 1·435 grams.

V.	Δ.	N.	M.
22·1	1·055	53·6	157
25·0	0·970	47·5	151
28·5	0·865	41·6	148
33·1	0·760	35·8	145

Acetanilide (M.W. = 135), 1·706 grams.

V.	Δ.	N.	M.
23·6	1·080	53·5	171
26·1	1·005	48·3	166
31·1	0·860	40·6	163
35·7	0·755	35·4	161
39·4	0·695	32·1	158

Acetamide (M.W. = 59), 1·710 grams.

V.	Δ.	N.	M.
23·4	1·690	124·0	110
28·2	1·565	102·8	99
34·7	1·340	83·6	94
39·6	1·170	73·1	94
44·3	1·075	65·4	91

Salicylamide (M.W. = 137), 0·591 gram.

V.	Δ.	N.	M.
24·0	0·420	18·0	149
27·4	0·370	15·7	149
32·9	0·320	13·1	143·5
38·5	0·265	11·2	148

Benzanilide (M.W. = 197), 1·761 grams.

V.	Δ.	N.	M.
22·8	0·965	39 2	205·5
26·0	0·865	34·3	201
30·0	0·740	29 8	203
37·3	0·585	24·0	207

Monochloroacetamide (M.W. = 93·5), 0·699 gram.

V.	Δ.	N.	M.
22·9	0·685	32·6	113·5
26·3	0·615	28·5	110
30·8	0·530	24·3	109
34·8	0·470	21·4	109
40·4	0·415	18·5	106

Solvent—Chloroform (continued).

Acetamide (M.W. = 59), 0·590 gram.

V.	Δ.	*N.*	*M.*
19·6	0·935	51·1	82
25·0	0·765	40·0	78·5
29·3	0·680	34·1	75
33·6	0·605	29·8	74

Trichloroacetamide (M.W. = 162·5), 1·953 grams.

V.	Δ.	*N.*	*M.*
20·0	1·175	60·0	211
22·9	1·085	52·5	201
28·5	0·895	42·0	195
33·1	0·785	36·3	191·5

Dichloroacetamide (M.W. = 128), 1·443 grams.

V.	Δ.	*N.*	*M.*
21·7	1·000	51·8	169
25·9	0·880	43·5	161
29·4	0·785	38·3	159
33·9	0·705	33·3	154

Trichlorolactamide (M.W. = 192·5), 1·145 grams.

V.	Δ.	*N.*	*M.*
18·2	0·590	32·7	272
22·5	0·515	26·4	251
26·9	0·460	22·1	235·5
31·6	0·425	18·8	217
45·4	0·305	13·1	211

Solvent—Ether.

Salicylamide (M.W. = 137), 0·463 gram.

V.	Δ.	*N.*	*M.*
21·3	0·455	15·9	148
22·8	0·425	14·8	148
24·8	0·390	13·7	149
26·4	0·365	12·8	149
31·8	0·305	10·6	148
33·6	0·290	10·1	147·5

Dichloroacetamide (M.W. = 128), 1·166 grams.

V.	Δ.	*N.*	*M.*
17·8	1·165	51·3	175
21·3	0·995	42·7	170·5
25·5	0·865	35·8	164
31·6	0·705	28·8	162

0·855 gram.

V.	Δ.	*N.*	*M.*
21·1	0·790	31·7	159·5
22·2	0·755	30·1	158
23·7	0·720	28·2	156
25·5	0·680	26·2	153

Trichlorolactamide (M.W. = 192·5), 1·875 grams.

V.	Δ.	*N.*	*M.*
15·9	1·015	61·3	360
17·4	0·960	56·0	348
22·9	0·780	42·5	325
26·9	0·695	38·7	310
32·9	0·605	29·6	292

Acetanilide (M.W. = 135), 0·475 gram.

V.	Δ.	*N.*	*M.*
23·6	0·360	14·9	173
24·9	0·340	14·1	173
28·6	0·295	12·3	174
32·5	0·260	10·8	174
34·3	0·250	10·2	171

Trichloroacetamide (M.W. = 162·5), 2·384 grams.

V.	Δ.	*N.*	*M.*
19·7	1·955	74·5	192
22·5	1·720	65·3	191
25·3	1·530	57·9	190
27·8	1·405	52·7	189
30·8	1·285	47·6	186

2·720 grams.

V.	Δ.	*N.*	*M.*
35·0	1·295	47·9	186
36·9	1·220	45·4	187
38·5	1·185	43·5	185

Solvent—Acetone.

Benzamide (M.W. = 121), 2·505 grams.

V.	Δ.	*N.*	*M.*
21·1	2·060	98·2	131
23·6	1·870	87·7	129
26·9	1·660	76·8	127
29·0	1·540	71·4	127
31·9	1·425	64·8	125

1·814 grams.

V.	Δ.	*N.*	*M.*
22·0	1·510	68·1	124
26·6	1·270	56·4	122
32·8	1·050	45·8	120
38·4	0·890	39·1	121
41·0	0·830	36·6	121

Benzanilide (M.W. = 197), 2·227 grams.

V.	Δ.	*N.*	*M.*
26·2	1·020	43·2	189
29·8	0·905	37·9	187
33·4	0·820	33·9	185
37·1	0·725	30·5	187

Monochloroacetamide (M.W. = 93·5), 2·654 grams.

V.	Δ.	*N.*	*M.*
29·5	2·075	96·3	99
31·4	1·965	90·3	97·5
33·6	1·855	84·5	97
37·0	1·695	76·7	96
40·2	1·575	70·6	95

Trichloroacetamide (M.W. = 162·5), 2·804 grams.

V.	Δ.	*N.*	*M.*
22·2	2·075	77·6	138
24·4	1·905	70·6	137
27·3	1·690	63·3	138
29·9	1·520	57·7	140
33·0	1·380	52·3	140

Carbamide (M.W. = 60), 0·247 gram.

V.	Δ.	*N.*	*M.*
37·4	0·235	11·0	64
39·6	0·225	10·4	63
41·7	0·210	9·9	64

Salicylamide (M.W. = 137), 2·100 grams.

V.	Δ.	*N.*	*M.*
24·5	1·690	62·5	115
28·1	1·460	55·0	116
32·1	1·255	48·0	118
35·0	1·145	44·0	119
38·1	1·035	40·0	121

Acetanilide (M.W. = 135), 1·777 grams.

V.	Δ.	*N.*	*M.*
23·4	1·410	56·3	122
26·6	1·235	49·5	123
29·3	1·120	44·9	123
33·0	1·005	39·9	122
36·5	0·890	36·0	124

Acetamide (M.W. = 59), 2·226 grams.

V.	Δ.	*N.*	*M.*
24·2	2·740	156·1	76
29·3	2·370	128·6	73
34·6	2·070	109·1	71
39·9	1·845	94·6	69
42·1	1·745	89·5	69

Dichloroacetamide (M.W. = 128), 1·768 grams.

V.	Δ.	*N.*	*M.*
24·9	1·430	55·5	113
27·2	1·295	50·8	114
29·9	1·170	46·2	115
33·3	1·040	41·4	116
37·0	0·930	37·3	117

Trichlorolactamide (M.W. = 192·5), 2·911 grams.

V.	Δ.	*N.*	*M.*
23·0	1·600	65·7	179
25·9	1·440	58·4	177
29·1	1·280	52·0	178
32·3	1·150	46·8	178
35·4	1·045	42·7	179
38·8	0·935	39·0	182

Solvent—Alcohol.

Benzamide (M.W. = 121), 1·240 grams.

V.	Δ.	*N.*	*M.*
21·0	0·765	48·9	123
24·6	0·645	41·6	124
28·9	0·555	35·4	123
32·3	0·515	31·7	118·5
37·5	0·420	27·3	125
42·4	0·370	24·2	126

Salicylamide (M.W. = 137), 1·542 grams.

V.	Δ.	*N.*	*M.*
29·6	0·615	38·0	135
32·6	0·555	34·6	135
36·2	0·495	31·1	137
42·1	0·430	26·8	136
45·9	0·395	24·5	135

Solvent—Alcohol (continued).

Acetanilide (M.W. = 135), 2·384 grams.

V.	Δ.	N.	M.
29·5	0·980	59·9	131
31·6	0·905	55·8	132
34·8	0·845	50·7	129
37·9	0·780	46·6	128
41·5	0·705	42·6	130
44·1	0·655	40·0	131

Acetamide (M.W. = 59), 1·347 grams.

V.	Δ.	N.	M.
23·4	1·570	97·6	58
25·4	1·450	90·0	58
27·5	1·340	82·9	58
30·5	1·205	74·8	58
35·7	0·995	63·9	60
39·3	0·910	58·1	60

Dichloroacetamide (M.W. = 128), 2·400 grams.

V.	Δ.	N.	M.
26·5	1·190	70·7	121
30·6	1·035	61·2	120·5
33·1	0·955	56·6	121
36·4	0·875	51·4	120
38·3	0·815	49·0	122
40·9	0·780	45·8	120

Trichlorolactamide (M.W. = 192·5), 2·130 grams.

V.	Δ.	N.	M.
24·5	0·775	45·1	178
28·0	0·675	39·5	178·5
31·6	0·600	35·0	179
35·9	0·530	30·8	179
41·0	0·460	27·0	179

Malonamide (M.W. = 102), 0·400 gram.

V.	Δ.	N.	M.
22·2	0·240	17·6	119
24·9	0·225	15·7	113·5
29·6	0·200	13·3	108
31·9	0·185	12·3	108

Benzanilide (M.W. = 197), 1·318 grams.

V.	Δ.	N.	M.
29·6	0·385	22·6	185
32·2	0·345	20·8	189
35·3	0·320	18·9	185·5
40·7	0·275	16·4	187
45·1	0·250	14·8	186

Monochloroacetamide (M.W. = 93·5), 2·058 grams.

V.	Δ.	N.	M.
27·2	1·250	80·9	96
29·1	1·160	75·5	97
32·0	1·065	68·8	96
35·1	0·985	62·8	95
39·4	0·870	55·8	95

Trichloroacetamide (M.W. = 162·5), 2·380 grams.

V.	Δ.	N.	M.
36·3	0·675	40·3	154
38·5	0·640	38·0	153·5
40·6	0·605	36·1	154
42·7	0·575	34·3	154
45·5	0·535	32·2	155

Carbamide (M.W. = 60), 1·860 grams.

V.	Δ.	N.	M.
29·6	1·445	104·7	69
32·0	1·355	96·9	68
34·4	1·275	90·1	67·5
37·1	1·175	83·5	68
40·3	1·110	76·9	66
42·6	1·055	72·7	66

Solvent—Water.

Benzamide (M.W. = 121), 2·720 grams.

V.	Δ.	N.	M.
20·5	0·380	119·7	184
24·2	0·335	92·9	177
28·5	0·295	78·8	172
32·3	0·265	69·6	169

Acetanilide (M.W. = 135), 1·897 grams.

V.	Δ.	N.	M.
32·3	0·140	43·5	222
33·4	0·150	42·0	201
36·0	0·130	39·0	215

0·7416 gram.

V.	Δ.	N.	M.
18·5	0·105	29·7	202
24·2	0·075	22·7	217

Salicylamide (M.W. = 137), 2·873 grams.

V.	Δ.	N.	M.
20·7	0·290	101·3	253
23·6	0·270	88·8	239
29·8	0·235	70·4	217
32·6	0·210	64·2	220

Acetamide (M.W. = 59), 2·716 grams.

V.	Δ.	N.	M.
22·2	1·125	207·1	57·5
24·4	1·005	188·4	59
26·8	0·910	171·4	59
29·1	0·835	157·9	59
34·7	0·675	132·6	62

Solvent—Water (continued).

Monochloroacetamide (M.W. = 93·5), 2·813 grams.

V.	Δ.	*N.*	*M.*
20·6	0·735	146·1	98·5
23·0	0·655	130·6	99
26·0	0·575	115·6	100
38·3	0·365	78·6	106

Trichlorolactamide (M.W. = 192·5), 2·805 grams.

V.	Δ.	*N.*	*M.*
19·1	0·355	76·0	218
21·4	0·325	68·0	214
24·2	0·285	60·0	214
26·5	0·270	55·0	208

Malonamide (M.W. = 102), 3·052 grams.

V.	Δ.	*N.*	*M.*
22·8	0·765	131·2	92·5
25·3	0·645	118·0	99
26·7	0·595	111·9	101
28·9	0·535	103·5	105
33·4	0·455	89·7	106

Dichloroacetamide (M.W. = 128), 1·800 grams.

V.	Δ.	*N.*	*M.*
19·0	0·360	74·0	139
22·8	0·280	61·7	149
26·3	0·240	53·5	152
29·7	0·210	47·4	154

Carbamide (M.W. = 60), 2·709 grams.

V.	Δ.	*N.*	*M.*
31·3	0·750	143·9	61
32·5	0·710	138·7	62
34·8	0·680	129·6	61
36·8	0·645	122·8	61
39·4	0·600	114·5	61

Discussion of Results.

The extent of the work with the eleven amides and the six solvents of which we had undertaken the study was determined chiefly by the solubility of the amides. For instance, boiling benzene dissolves so little acetamide that the consequent rise in boiling point is too small for accurate measurement. We have carried out measurements: (1) in all cases where the amide is soluble enough to cause a rise of about 0·25° at least; (2) for special reasons in two or three cases where the maximum rise was less than this. The poorest solvent is ether.

The results have been confirmed by duplicate experiments, and where the results are abnormal, by repeated experiments. We thought it sufficient, in each case, to quote a single series of data.

The discussion of results is divided into three sections: I. The action of the solvent in allowing or preventing association of the solute. II. The tendency of the amides to association. III. The constitution of the amides.

I. *The Action of the Solvent in Allowing or Preventing Association of the Solute.*

In what follows, it being understood that the line between association and non-association is not always easy to draw, doubtful cases will be specially mentioned. As a rule we have assumed that an increase in the molecular weight of not less than 10 per cent. is an indication of association.

(1) Benzene: every amide investigated, unless perhaps benzanilide, is associated.

(2) Ether: only salicylamide is unassociated. (The saturated solution of salicylamide, however, contains only 16 milligram-molecules per 100 c.c., and so weak a solution cannot be a good test of the tendency of the amide.)

(3) Chloroform: only salicylamide and benzanilide are unassociated.

(4) Acetone: only acetamide is associated.

(5) Alcohol: this solvent gives as nearly as possible simple molecules. Carbamide and malonamide show signs of association, but only to a small extent.

(6) Water: acetamide,* monochloroacetamide, carbamide, and malonamide are unassociated; trichlorolactamide is a doubtful case; benzamide, salicylamide, acetanilide, and dichloroacetamide are associated.

As one way of showing the bearing of these results on the Nernst-Thomson theory of association, the following table has been prepared. It consists (1) of a summary of our results; (2) the dielectric constants of the solvents:

Solvent.	Benzene.	Ether.	Chloroform.	Acetone.	Alcohol.	Water.
Number of amides investigated...	8	5	9	10	11	9
,, ,, which form simple molecules	1 doubtful	1	2	9	9	4 and 1 doubtful
,, ,, which yield associated molecules	7	4	7	1	2 doubtful	4
Dielectric constant of solvent ...	2·3 at 18°	4·4 at 18°	5 at 22°	25 at 20°	26 at 20°	80 at 17°

A consideration of this table leads us to the conclusion that the action of the solvent, water excepted, in permitting, or preventing, association of the solute is connected with the dielectric constant in the way which the Nernst-Thomson theory predicts. The smaller the dielectric constant of the solvent the greater is the association of the solute. Ether, which is usually described as regards its effect on the solute as being non-associating, deserves particular notice. Our results show that, as theory predicts from the low dielectric constant, ether leads to association of the solute.

In order to examine, as nearly as possible under comparable conditions, the action of benzene, ether, and chloroform in allowing association, the following method was adopted.

---

* In the preliminary note on this work, acetamide was mentioned, by a mistake, as being associated in aqueous solution.

The molecular weights and the association factors of as many amides as possible were calculated at a certain concentration of solution. This concentration should be fixed on, so that, whilst the elevation of the boiling point of the solution is large enough to admit of being accurately measured, the solution can still be regarded as "dilute," and, further, so that what extrapolation is required is reduced to a minimum. The concentration fixed on as satisfying these requirements is 30 milligram-molecules per 100 c.c. (the molecular weight, of course, being the same as the formula weight).

$$\text{The association factor} = \frac{\text{molecular weight in solution}}{\text{formula weight}}.$$

Amide.	Molecular weights in			Association factors in		
	Benzene.	Ether.	Chloroform.	Benzene.	Ether.	Chloroform.
Benzamide	184	—	140	1·52	—	1·16
Salicylamide	186	148	148·5	1·36	1·08	1·08
Acetanilide	205	174	156	1·52	1·30	1·16
Benzanilide	228	—	201	1·17	—	1·0
Acetamide	—	—	75	—	—	1·27
Monochloroacetamide	130	—	112	1·39	—	1·20
Dichloroacetamide	178	160	150	1·39	1·25	1·17
Trichloroacetamide	210	187	191	1·29	1·15	1·17
Trichlorolactamide	294	292	261	1·52	1·52	1·35

Walker (*Introduction to Physical Chemistry*, 1907, p. 204), in discussing the connexion between the nature of the solvent and association of the solute, puts ether together with acetone, and throws these two solvents into contrast with "benzene and chloroform, in which the tendency to association is considerable." According to our figures, association is always greater in benzene than in chloroform. The figures for ether, limited as they are, show that association in ether tends to be less than in benzene, much the same as in chloroform, and much greater than in acetone.

In accordance with the high dielectric constants of acetone and alcohol, association in these solvents is rare. The case of water as a solvent is remarkable.

On the Nernst-Thomson theory, the dielectric constant of water (more than three times that of acetone or alcohol) should lead to the complete absence of association in aqueous solution, whilst actually four substances are found to be associated, namely, benzamide, salicylamide, acetanilide, and dichloroacetamide. These four are the only instances known to us of a substance having a higher molecular weight in water than in alcohol.

We do not maintain that the data for acetanilide are very accurate, the small elevation of boiling point of the solution, consequent on the comparatively small solubility of the anilide, precludes this. Hence there must be uncertainty as to the degree of association, but that there is association we have no doubt.

Certain possibilities, other than association in water, a very rare occurrence, deserved to be noticed in passing. The amide may distil over with the steam, which would cause a gradual rise in molecular weight of somewhat the same kind as is actually found in the case of dichloroacetamide.

An experiment instituted to test this point showed that dichloroacetamide does not distil with steam, and is not decomposed by continuous boiling with water for forty minutes.* Again, the amide may undergo ionisation, or it may be hydrolysed, or it may combine with water without the occurrence of hydrolysis. The possibility of ionisation, as a matter of fact, is apparently negligible, since Hantzsch and Buchner (*Ber.*, 1901, **34**, 3147) found that the amides are very feeble electrolytes, and Fawsitt (*Proc. Roy. Soc. Edin.*, 1904, **25**, 60) declares that "the non-conductivity of the amides in aqueous solution is a good criterion of their purity." Again, Crocker (Trans., 1907, **91**, 608), in the course of work on the hydrolysis of aliphatic amides, was led to think that an amide must combine with water before hydrolysis can proceed. Acetamide, for example, is hydrated thus:

$$CH_3{\cdot}CO{\cdot}NH_2 + H_2O \rightleftharpoons CH_3{\cdot}CO{\cdot}NH_3{\cdot}OH.$$

Should any one of these possibilities be realised, the consequence would be an increase in the elevation of the boiling point, whilst association means a decrease. It is therefore impossible to explain in terms of ionisation (without or with hydrolysis), or of combination with water, the results which we adduce as proofs of association. Indeed, in so far as these phenomena occur, the effect due to association is masked, and the degree of association must be even greater than our figures show.

II. *The Tendency of the Amides to Association.*

The Nernst-Thomson theory indicates that association which is considerable in amount in a solvent of low dielectric constant is diminished when the solvent has a high dielectric constant. Inasmuch as certain substances which are not associated in alcohol solution are found to be associated in water, a substance of much higher dielectric constant, it is obvious that these cases do not come within the scope of the theory. Nevertheless, we do not advance these instances as so many objections to the theory, with which, indeed, our results in the case of five solvents are in good agreement. On consideration, it becomes obvious that the theory makes the assumption, although

---

* Trichloroacetamide, when boiled with water, shows very obvious signs of decomposition in the course of five minutes.

Nernst omits to mention it, that association is due to electrical forces, which are supposed to be modified according to the dielectric constant of the solvent. We can only suppose that in the four cases which fall outside the theory, the association is not due to this cause; that is, association is due sometimes to one cause and sometimes to another.

In addition to the evidence derived from the behaviour of the amides in solution, there is evidence of another kind, namely, that they have a tendency to association. This is to be found in the existence of the substances: $2CH_3{\cdot}CO{\cdot}NH_2,HCl$, $2CH_3{\cdot}CO{\cdot}NH_2,NaBr$ (Titherley, Trans., 1901, **79**, 413), $2CH_3{\cdot}CO{\cdot}NH_2,NaI$, $2CH_3{\cdot}CH_2{\cdot}CO{\cdot}NH_2,HCl$, $3COPh{\cdot}NH_2,2HCl$, &c. The question whether the production of the substance $3COPh{\cdot}NH_2,2HCl$ is due to the "forces electrical in their origin," which cause association of benzamide in benzene, or to the factor, whatever it may be, which causes association of benzamide in water, can only be left for further consideration.

Meantime, we would place on record our conviction of the necessity in investigations into the amides and allied compounds, especially of their physical properties (compare Frankland and Twiss, Trans., 1906, **89**, 1852; Pickard and Littlebury, Trans., 1907, **91**, 300), of taking into account their strong tendency to association. According to our results, the most suitable solvent in such investigations is ethyl alcohol.

III. *The Constitution of the Amides.*

The amides in general may be represented by the ordinary formula $R{\cdot}CO{\cdot}NH_2$, or the hydroxylic formula $R{\cdot}C(OH){:}NH$, and Auwers' series of researches on the amides was begun in the hope of deciding between the two formulæ. Although the usual assumption is that association is due to the hydroxyl group, we can say that the assumption is not established by our results. If the constitution of benzamide is $C_6H_5{\cdot}C(OH){:}NH$ and that of acetamide $CH_3{\cdot}CO{\cdot}NH_2$, and the evidence of organic chemistry is in favour of these formulæ (Tafel and Enoch, *Ber.*, 1890, **30**, 103, 1550), then, on the hydroxylic theory of association, benzamide should show a greater tendency to association than acetamide. Actually, at the same equivalent concentration in chloroform solution, the association factor of benzamide is 1·16, and that of acetamide 1·27. Hence the tendency of the amides to association cannot be regarded as furnishing positive proof that they are hydroxylic compounds. Moreover, it is doubtful if the determination of the molecular complexity of the amides can do much towards settling the question of their constitution.

At the present day, it is a pity that the discussion of the association problem should sometimes be cut short by a mere invocation of the hydroxyl group, as if that were the only and the final cause of association. After all, the tervalent nitrogen atom, or the oxygen atom of the group $\cdot CO\cdot NH_2$, may have as much to do with the association of amides as the oxygen atom of a hydroxyl group. There is, as a matter of fact, a strong body of opinion against the hydroxylic constitution of the amides, and in favour of the ordinary method of formulation. Claisen (*Annalen*, 1895, **287**, 360) abandoned the formula $C_6H_5\cdot N\colon CH\cdot OH$ for formanilide in favour of $C_6H_5\cdot NH\cdot CHO$. Auwers (*Zeitsch. physikal. Chem.*, 1897, **23**, 468; *Ber.*, 1901, **34**, 3538), Hantzsch, Voegelen, and Buchner (*Ber.*, 1901, **34**, 3142, 3147), Hantzsch and Dollfus (*Ber.*, 1902, **35**, 226), Schmidt (*Ber.*, 1903, **36**, 2459), and Fawsitt (*Proc. Roy. Soc. Edin.*, 1904, **25**, 60) in various ways come, one and all, to the conclusion that the formula $R\cdot CO\cdot NH_2$ is preferable to $R\cdot C(OH)\colon NH$.

In continuation of the work, we propose to ascertain the molecular complexity of other amides in various solvents, and, in connexion with this, the effect on the molecular weight determination of change of volume during solution will be investigated.

The phenomenon of increase of molecular weight of the solute as the solution becomes more dilute is due, according to Arrhenius, to combination between solute and solvent. We have obtained indications of this phenomenon, for instance, with dichloroacetamide in water, and salicylamide in acetone, which we propose to investigate.

We would thank Professor Japp, of the University of Aberdeen, for the loan of a Landsberger thermometer, of which we found ourselves unexpectedly in need. The expenses of the work have been met in part by a grant made to one of us by the Executive Committee of the Carnegie Trust for the Universities of Scotland.

CHEMICAL DEPARTMENT,
UNIVERSITY OF SHEFFIELD.

LXXXIII.—*The Constituents of Olive Leaves.*

By FREDERICK BELDING POWER and FRANK TUTIN.

THE leaves of the olive tree, *Olea Europaea*, Linné, were employed many years ago as a remedy in intermittent fever, and quite recently have again been brought to notice on account of their reputed therapeutic value as a tonic and febrifuge (*Pharm. J.*, 1906, **77**, 376).

The only recent investigation of these leaves that has been recorded appears to be that of F. Canzoneri (*Gazzetta*, 1906, **36**, ii, 372).

This author extracted the leaves with 95 per cent. alcohol, and observed that the liquid, on cooling, deposited small quantities of crystals, consisting apparently of two wax-like substances melting at 85—100° and 69—70° respectively. From the alcoholic liquid, he obtained a white compound, $C_{25}H_{44}O_3$ or $C_{24}H_{42}O_3$ (m. p. 297—298°), soluble in ether; a white, crystalline, resin-like substance (m. p. 253—255°); a substance melting at about 236°; a crystalline acid (m. p. 165°) insoluble in ether; a substance melting at 180° when crystallised from acetic acid, and at 200—235° after recrystallisation from alcohol; an acid of dough-like consistence, turning brown on exposure to the air, together with mannitol, gallic and tannic acids.

It is evident that the above-mentioned products were, for the most part, of a very indefinite character, and that they did not represent pure substances. The compound $C_{25}H_{44}O_3$ or $C_{24}H_{42}O_3$, melting at 297—298°, would appear, however, to have been the hydrated form of a substance having the formula $C_{31}H_{50}O_3$ (m. p. 303—304°), which the present authors have isolated and designated *oleanol*, since compounds possessing the formulæ $C_{24}H_{42}O_3$ and $C_{31}H_{50}O_3,H_2O$ respectively have approximately the same percentage composition.

For the purpose of ascertaining more precisely the nature of the constituents of olive leaves, their complete investigation was undertaken, and the results are embodied in the present communication.

EXPERIMENTAL.

The material employed in this investigation consisted of the leaves of *Olea Europaea*, Linné, which had been freshly gathered for us during the early spring in the neighbourhood of Ventimiglia, on the Italian Riviera.

A portion of the leaves was first tested for the presence of an alkaloid, but with a negative result.

In order to ascertain the general characters of the constituents of the leaves, 50 grams of the ground material were successively extracted in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried at 100°, were obtained:

Petroleum (b. p. 35—50°)	extracted	2·86	per cent.
Ether	,,	7·16	,,
Chloroform	,,	1·00	,,
Ethyl acetate	,,	6·26	,,
Alcohol	,,	12·56	,,
	Total	29·84	,,

For the purpose of a complete examination, a quantity (28·35 kilograms) of the ground leaves was extracted by continuous percolation with hot alcohol. One kilogram of the resulting extract, containing 567 grams of extracted matter, was then mixed with water and distilled with steam, when a trace of an aromatic essential oil was obtained. The mixture contained in the distillation flask was filtered while hot, and a quantity (163·5 grams) of a pulverulent, green resin (*A*) thus collected, which was washed with boiling water, and dried. The combined filtrate and washings, on cooling, deposited 47 grams of brown, resinous matter (*B*), which was also collected on a filter, freed from substances soluble in cold water, and dried. The final aqueous filtrate and washings (*C*), which amounted to about 10 litres, were then concentrated on a water-bath to about one-fourth this volume.

Examination of the Green Resin (*A*).

This resin, which was in the form of a green powder, was mixed with a considerable quantity of purified sawdust, and the mixture subjected to prolonged successive extraction in a large Soxhlet apparatus with the following solvents: petroleum (b. p. 35—50°), ether, chloroform, ethyl acetate, and alcohol.

Petroleum Extract of the Resin.

The material removed by petroleum was dark green, and weighed 41 grams. A portion of it was very sparingly soluble in this solvent. The entire petroleum extract was dissolved in 700 c.c. of warm ether, and the solution cooled, when about 3 grams of a solid substance separated. This was collected on a filter and washed with cold ether, after which it was distilled under a pressure of 15 mm. The distillate, which rapidly solidified, was crystallised from ethyl acetate, when small, glistening, colourless leaflets were obtained, which melted at 74·5°:

0·0872 gave 0 2717 CO_2 and 0·1148 H_2O. C = 85·0 ; H = 14·6.

$C_{35}H_{72}$ requires C = 85·4 ; H = 14·6 per cent.

This substance, therefore, was pentatriacontane.

The ethereal filtrate from the pentatriacontane was shaken with a solution of sodium hydroxide, when a dark green, flocculent product separated, which was collected on a filter and thoroughly washed with ether. The filtered, alkaline, aqueous liquid yielded nothing on acidification. For the examination of the green, flocculent product, it was warmed for some time with dilute aqueous sulphuric acid and chloroform, after which the chloroformic liquid was separated, washed, and evaporated to dryness. The small amount of residue was dissolved in ethyl acetate, and the solution heated with animal charcoal and filtered, when, on allowing the liquid to cool, small, colourless crystals were obtained. These melted quite indefinitely between 230° and

270°, and were found to be a mixture, for, when heated with acetic anhydride, they yielded diacetyloleanol, a substance which will subsequently be described, together with an acetyl derivative melting at 83·5°. The latter substance crystallised from acetic anhydride or ethyl acetate in tufts of small needles, but the amount obtained was not sufficient for analysis.

Isolation of a New Monocarboxylic Acid, $C_{22}H_{45}\cdot CO_2H$.

The ethereal liquid, which had been shaken with sodium hydroxide solution, was washed with water, when a large amount of chlorophyll was removed. This was examined, but nothing definite could be isolated from it. The ethereal liquid was then evaporated, and the residue heated with an alcoholic solution of an excess of potassium hydroxide for one hour in a reflux apparatus. After removing the alcohol, water was added, and the mixture extracted eleven times with ether. During the first extraction, a flocculent precipitate collected in the lower part of the ethereal layer. This was separated, washed, treated with sulphuric acid, and the product extracted with chloroform. On removing the chloroform, a wax-like residue was obtained, which, after treatment with animal charcoal, was crystallised from ethyl acetate, from which it separated in small, colourless, glistening leaflets melting at 68—69°:

0·1047 gave 0·2993 CO_2 and 0·1223 H_2O. C = 78·0 ; H = 13·0.
0·0959 „ 0·2738 CO_2 „ 0·1125 H_2O. C = 77·9 ; H = 13·0.
$C_{23}H_{46}O_2$ requires C = 78·0 ; H = 13·0 per cent.

This substance therefore appears to be a new *monocarboxylic acid*, as no acid possessing the formula $C_{23}H_{46}O_2$ has heretofore been described.

The combined ethereal extracts of the alkaline liquid were washed, dried, and concentrated to a small bulk, when a quantity of crystalline leaflets separated. These were removed, and, on further concentrating the solution, three more successive crops of crystals were obtained from it. The first and second portions of crystalline material, when dry, melted at 68°. They were therefore mixed and distilled in a vacuum, when a distillate was obtained which solidified and, when crystallised from ethyl acetate, separated in handsome, nacreous leaflets melting at 68—68·5°:

0·0862 gave 0·2697 CO_2 and 0·1147 H_2O. C = 85·3 ; H = 14·8.
$C_{31}H_{64}$ requires C = 85·3 ; H = 14·7 per cent.

The first crops of crystals therefore consisted of hentriacontane.

The third portion of crystalline material, when dissolved in chloroform, gave with acetic anhydride and sulphuric acid the colour reaction characteristic of the phytosterols, but it also contained hentriacontane, and no pure substance could be isolated from it.

Isolation of a New Crystalline Alcohol, Oleasterol, $C_{20}H_{33}\cdot OH$.

The last portion of crystals which separated from the above-described ethereal liquid was recrystallised several times from ethyl acetate when tufts of needles were obtained which melted at 172°. It was then crystallised twice from benzene, from which it finally separated in small tufts of fine needles melting at 174°:

0·0969 gave 0·2938 CO_2 and 0·1023 H_2O. C = 82·7; H = 11·7.

$C_{20}H_{34}O$ requires C = 82·8; H = 11·7 per cent.

This substance is evidently an alcohol related to the phytosterols, but is not identical with any compound previously described. It is therefore proposed to designate it *oleasterol*.

If a small quantity of oleasterol is dissolved in chloroform, a little acetic anhydride added, and, after first boiling the solution and then cooling it, a drop of concentrated sulphuric acid introduced, a slight yellow colour is first developed, which rapidly changes to pink. The tint then deepens to an intense magenta colour, which is accompanied by a brilliant yellowish-bronze fluorescence, subsequently changes to violet, and, after about one hour, the liquid becomes dull blackish-brown. If the reaction is conducted in acetic anhydride solution, no chloroform being used, the same colours are produced, but the changes are more rapid. When concentrated sulphuric acid is added to a solution of oleasterol in chloroform, the acid layer becomes yellow and, finally, of a deep orange colour. Solid oleasterol, when brought in contact with a drop of concentrated sulphuric acid, develops a bright orange and, finally, a vermillion-red colour, but again becomes colourless on the addition of water. Oleasterol is isomeric with several alcohols which possess properties similar to those of the phytosterols, namely, cinchol, cupreol, quebrachol, and rhamnol (compare Beilstein's *Handbuch*, 3rd edit., II., 1068, and *Proc. Amer. Pharm. Assoc.*, 1904, **52**, 296), but melts at a higher temperature than any of these compounds, and differs from the last-named one, with which it has been directly compared, both in appearance and in the colour reactions yielded by it.

On removing the solvent from the original ethereal mother liquors from which the oleasterol had been separated, a residue was obtained which amounted to about 4 grams. This was distilled under 12 mm. pressure, when it passed over for the most part between 300° and 365° without decomposition, but a portion distilled above this temperature. The distilled product was dissolved in boiling ethyl acetate, when, on cooling the solution, very hard, crystalline, wart-like masses separated, which melted at 200—204°. After several recrystallisations from ethyl acetate and, finally, from benzene, the melting point of the substance remained constant at 209—210°:

0·0864 gave 0·2560 CO_2 and 0·0896 H_2O. C = 80·8; H = 11·5.
$C_{27}H_{46}O_2$ requires C = 80·6; H = 11·4 per cent.

This substance was identical with a new compound, *homo-olestranol*, which was subsequently isolated in larger quantity from the ether extract of the resin.

The alkaline, aqueous liquid, from which the above-described alcohols and hydrocarbon had been removed by means of ether, was acidified with sulphuric acid and distilled with steam, but no volatile product was obtained. The acid liquid was therefore extracted with ether, the ethereal solution concentrated to a small bulk, and a considerable volume of light petroleum added. This caused the precipitation of the greater portion of the dissolved material in the form of an amorphous, dark green powder, from which nothing crystalline could be obtained. The clear petroleum liquid was decanted from the precipitate and evaporated, when a residue was obtained which was distilled under diminished pressure. The distilled product amounted to about 4 grams, and yielded a small quantity of a mixture of fatty acids melting at 46—49°, but the greater portion consisted of an oily liquid, which was unsaturated, and probably contained oleic acid.

Ethereal Extract of the Resin.

This extract amounted to 87 grams. As originally obtained, it consisted of a dark green, ethereal solution containing a quantity of an amorphous, green, sparingly soluble powder. The latter was collected on a filter and washed well with ether, after which it weighed 33 grams. On concentrating the ethereal filtrate to about 500 c.c., a further quantity (20 grams) of a similar amorphous powder was obtained.

Isolation of a New Crystalline Substance, Oleanol, $C_{31}H_{48}O(OH)_2$.

The above-mentioned portions of solid matter were separately examined, but were found to be identical. The material was dissolved in hot alcohol, and the solution decolorised by means of animal charcoal, after which it deposited a colourless substance in tufts of extremely fine, silky needles. This substance, when not quite pure, tends to separate in an amorphous condition, and, in these circumstances, can most readily be obtained crystalline by allowing its solution in boiling alcohol to evaporate. By successively concentrating the mother liquors from this crystalline substance, further quantities of it were obtained, and also some portions of amorphous material which could not be caused to crystallise from any solvent. It was at first thought that these amorphous products might contain a second substance, but on acetylation they gave an almost quantitative yield of the diacetyl derivative of the crystalline substance, with only a little amorphous matter. As first obtained, the crystalline substance melted at about 301°, but on recrystallisation the melting point was raised to 303—304°, when it remained constant, no decomposition occurring. After drying at 110°, it was analysed:

0·1127 gave 0·3271 CO_2 and 0·1088 H_2O. C = 79·1; H = 10·7.
0·1135 „ 0·3291 CO_2 „ 0·1083 H_2O. C = 79·1; H = 10·6.
$C_{31}H_{50}O_3$ requires C = 79·1; H = 10·6 per cent.

No substance of the formula $C_{31}H_{50}O_3$ has previously been described, and it is therefore proposed to designate the new compound *oleanol*.

Oleanol is not very soluble in any of the usual organic solvents, but is moderately so in boiling chloroform, from which it separates in an amorphous condition. When crystallised from ordinary alcohol, it contains one molecule of water of crystallisation, as shown by the following analysis:

0·3466 of air-dried substance, on heating at 110°, lost 0·0130 H_2O. H_2O = 3·7
0·1136 of air-dried substance gave 0·3152 CO_2 and 0·1107 H_2O. C = 75·7; H = 10·8.
$C_{31}H_{50}O_3,H_2O$ requires H_2O = 3·7; C = 76·2; H = 10·7 per cent.

Two of the oxygen atoms contained in oleanol are, as shown below, present in the form of hydroxyl groups, and one of the latter possesses phenolic properties. In consequence of this fact, the substance reacts with sodium carbonate and hydroxide, giving an insoluble, amorphous *sodium* derivative. The third oxygen atom present in oleanol probably occurs in an ether linking, since the compound does not react with hydroxylamine. It was ascertained, however, by means of Perkin's modification of Zeisel's method, that no methoxyl or ethoxyl group was present. When oleanol is gently warmed with concentrated sulphuric acid, a deep orange colour is produced, and, when dissolved in chloroform, it does not decolorise a solution of bromine in the same solvent.

A determination of the specific rotatory power of oleanol gave the following result:

0·3032, dissolved in 25 c.c. of chloroform at 30°, gave α_D +1°54′ in a 2-dcm. tube, whence $[\alpha]_D$ +78·3°.

Diacetyloleanol, $C_{31}H_{48}O_3(CO\cdot CH_3)_2$.—A quantity of oleanol was dissolved in acetic anhydride, and the solution boiled for some time.

It was then allowed to cool, when the acetyl derivative separated in colourless, glistening leaflets:

0·0994 gave 0·2749 CO_2 and 0·0881 H_2O. C = 75·4; H = 9·8.

$C_{31}H_{48}O_3(CO{\cdot}CH_3)_2$ requires C = 75·8; H = 9·7 per cent.

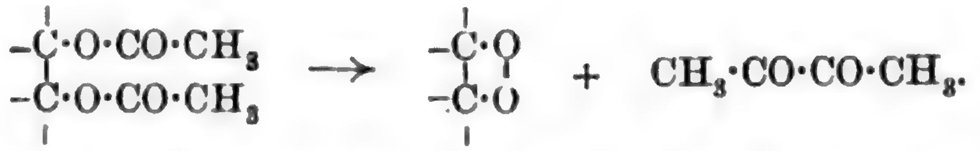
Diacetyloleanol is very readily soluble in chloroform, only moderately so in ethyl acetate, and nearly insoluble in cold alcohol. It is recrystallised most conveniently from acetic anhydride.

When diacetyloleanol is heated, fusion takes place at about 208°, the exact temperature depending on the rate of heating, gas is then evolved, and the liquid quickly re-solidifies. The solid so obtained is insoluble in alcohol, and only sparingly soluble in ethyl acetate or acetic anhydride, and is not acted on by the latter. It is very readily soluble in chloroform or benzene, but crystallises from a mixture of one part of the latter and two parts of petroleum (b. p. 90—120°) in small tufts of colourless needles, which do not melt at a temperature of 310°. This *substance* is unaffected by alkalis, and, when dissolved in chloroform, slowly decolorises a solution of bromine in the same solvent. On analysis, it yielded the following results:

0·1128 gave 0·3280 CO_2 and 0·1063 H_2O. C = 79·3; H = 10·5.
0·1049 „ 0·3058 CO_2 „ 0·0990 H_2O. C = 79·5; H = 10·5.

$C_{31}H_{48}O_3$ requires C = 79·4; H = 10·3 per cent.

This result indicates that, on heating diacetyloleanol, both the acetyl groups are removed, but, as no water is present during the operation, they are not eliminated by hydrolysis. The change might be represented as follows:



This view is in harmony with the fact that the high melting product contains no hydroxyl group, and the loss of weight suffered by the original acetyl derivative on being heated is also in agreement with it:

0·1648 of diacetyloleanol, on heating at 230°, lost 0·0254 $CH_3{\cdot}CO$. $CH_3{\cdot}CO$ = 15·4.

$C_{31}H_{48}O_3(CO{\cdot}CH_3)_2$ requires $CH_3{\cdot}CO$ = 15·5 per cent.

Monoacetyloleanol, $C_{31}H_{48}O_2(OH){\cdot}CO{\cdot}CH_3$.—A quantity of diacetyloleanol was dissolved in 85 per cent. alcohol, and the solution boiled for forty-five minutes. On cooling the liquid, a product was obtained which crystallised in needles melting at 258°. This substance was much more soluble in alcohol than diacetyloleanol, and was evidently a *monoacetyloleanol*, since it readily yielded the diacetyl derivative on treatment with acetic anhydride. After drying at 110°, it was analysed:

0·1055 gave 0·2978 CO_2 and 0·0980 H_2O. C = 77·0 ; H = 10·3.

$C_{33}H_{52}O_4$ requires C = 77·3 ; H = 10·2 per cent.

Oleanol possesses some phenolic properties, as indicated by the fact that it yields a sodium derivative. The hydroxyl group contained in the above-described monoacetyloleanol is, however, devoid of such properties, since the compound does not react with cold alkalis.

Monomethyloleanol, $C_{31}H_{48}O(OH)\cdot O\cdot CH_3$.—Five grams of oleanol were dissolved in absolute alcohol, and a slight excess of both sodium ethoxide and methyl iodide added. The mixture was then heated for one and a-half hours in a flask attached to a reflux condenser, after which the greater part of the solvent was removed. The addition of water then caused the precipitation of a *monomethyloleanol*, which crystallised from alcohol in long, thin, quite colourless needles. This compound, when dried in the air at the ordinary temperature or at 90°, melted at about 145° and then re-solidified, after which it fused at 194—195°. It also melted sharply at the latter temperature when dried at 120°. After drying at 125°, it gave on analysis the following results :

0·1325 gave 0·3828 CO_2 and 0·1290 H_2O. C = 78·8 ; H = 10·8.

0·3144 gave, by Perkin's modification of Zeisel's method, 0·1500 AgI. $O\cdot CH_3$ = 6·3.

$C_{32}H_{52}O_3$ requires C = 79·3 ; H = 10·7 ; $O\cdot CH_3$ = 6·4 per cent.

The air-dried preparation was then analysed :

0·0977 gave 0·2788 CO_2 and 0·0960 H_2O. C = 77·8 ; H = 10·9.

0·3169, on heating at 125°, lost 0·0139 $C_2H_5\cdot OH$. $C_2H_5\cdot OH$ = 4·4.

$C_{31}H_{48}O(OH)\cdot O\cdot CH_3,\frac{1}{2}C_2H_5\cdot OH$ requires C = 78·1 ; H = 10·8 ; $C_2H_5\cdot OH$ = 4·5 per cent.

Acetylmethyloleanol, $C_{31}H_{48}O_2(O\cdot CH_3)\cdot CO\cdot CH_3$.—Monomethyloleanol was dissolved in acetic anhydride, and the mixture boiled for half an hour. The solution was then allowed to cool, when *acetylmethyloleanol* separated in long, highly lustrous leaflets, which melted at 215·5° :

0·1041 gave 0·2960 CO_2 and 0·0978 H_2O. C = 77·5 ; H = 10·4.

$C_{34}H_{54}O_4$ requires C = 77·6 ; H = 10·3 per cent.

0·2132, on hydrolysis, neutralised 4·4 c.c. $N/10$ NaOH.

$C_{31}H_{48}O_2(O\cdot CH_3)\cdot CO\cdot CH_3$ requires 4·1 c.c.

Acetylmethyloleanol can be recrystallised from ordinary alcohol, but, when boiled for some time with this solvent, the acetyl group is eliminated and monomethyloleanol is regenerated.

The original ethereal filtrate from the crude oleanol was shaken with a solution of ammonium carbonate, but this treatment removed only small amounts of amorphous products. It was then shaken with several successive portions of a solution of sodium carbonate, when a considerable quantity of a green precipitate was formed. This precipitate was separated from the ethereal liquid and from the alkaline, aqueous solution, when, on examination, it was found to consist almost entirely of sodium oleanol, together with chlorophyll. The alkaline, aqueous liquid was acidified, but it yielded only a small amount of tarry matter. The ethereal liquid, when free from substances which reacted with sodium carbonate, was shaken with a solution of sodium hydroxide, but this dissolved nothing. It was then washed with water, when a large amount of chlorophyll was removed, dried, and the greater part of the ether evaporated.

Isolation of Two New Crystalline Alcohols.

Olestranol, $C_{25}H_{42}O_2$, *and Homo-olestranol*, $C_{27}H_{46}O_2$.

On allowing the concentrated ethereal liquid, obtained as above described, to stand, it deposited about 3 grams of a white solid. This was dissolved in hot ethyl acetate, from which, on cooling, it separated in hard, wart-like masses, which melted at 217°. After recrystallisation from benzene, it melted at 217—218° and was analysed:

0·0998 gave 0·2928 CO_2 and 0·1009 H_2O. C = 80·0; H = 11·2.
0·0813 „ 0·2389 CO_2 „ 0·0845 H_2O. C = 80·1; H = 11·4.
$C_{25}H_{42}O_2$ requires C = 80·2; H = 11·2 per cent.

This substance, so far as can be ascertained, is not identical with any compound previously described. It is proposed therefore to designate it *olestranol*, since it is an alcohol.

Olestranyl acetate and *benzoate* were prepared, but were found to be uncrystallisable syrups. The latter compound was very viscid, and dissolved readily in ethyl acetate and in chloroform, but was almost insoluble in alcohol. When dissolved in chloroform and treated with a solution of bromine in the same solvent, olestranol readily gives a *bromide*, which is precipitated as a viscid oil. This oil did not become crystalline on standing, and when warmed with any solvent, in order to bring it into solution, it evolved hydrogen bromide, yielding a product which was readily soluble in chloroform, but uncrystallisable. Olestranol exhibits colour reactions which, so far as could be observed, are indistinguishable from those shown by oleasterol (p. 895). Its formula, $C_{25}H_{42}O_2$, indicates it to be a lower homologue of a hydroxyphytosterol, and its properties are in accordance with this view, for, although some of the colours which are produced on treating it with acetic anhydride and sulphuric acid differ from those given under similar conditions by the phytosterols, the general character of the colour reactions is analogous to that yielded by the latter compounds.

The original ethereal filtrate from the olestranol was green, owing to the presence of chlorophyll. It was therefore boiled with an alcoholic solution of potassium hydroxide, the greater part of the solvent removed, water added, and the mixture extracted six times with ether. On removing the solvent, several grams of a light-coloured product were obtained. This was repeatedly crystallised from ethyl acetate, from which it separated in hard, wart-like masses, identical in appearance with the nodular masses of olestranol obtained under similar conditions. This preparation, however, melted at a temperature lower than that at which olestranol fuses, namely, at 210°, and repeated crystallisations from ethyl acetate and from benzene failed to raise the melting point of the material:

0·1120 gave 0·3314 CO_2 and 0·1152 H_2O. $C = 80·7$; $H = 11·4$.
$C_{27}H_{46}O_2$ requires $C = 80·6$; $H = 11·4$ per cent.

This compound, melting at 210°, is therefore identical with the substance possessing the same formula and melting point which was isolated in smaller quantity from the petroleum extract of the resin. Its formula, $C_{27}H_{46}O_2$, is that of a hydroxyphytosterol, and, since it is not identical with any compound previously described and is apparently a homologue of olestranol, differing from the latter by the increment of the elements C_2H_4, the name *homo-olestranol* may appropriately be assigned to it.

One compound, possessing properties similar to those of homo-olestranol, has previously been isolated from the seeds of *Casimiroa edulis*, La Llave (Fam. *Rutaceae*), by W. Bickern (*Arch. Pharm.*, 1903, **241**, 173). This substance, which has been designated casimirol, has been assigned the formula $C_{27}H_{48}O_2$, and is stated to melt at 207°. It was therefore at first thought that these two substances might be identical, but a comparison of their respective colour reactions rendered it evident that this was not the case.

Homo-olestranol exhibits colour reactions which, like those of olestranol, are identical with those yielded by oleasterol. It is apparently somewhat more readily soluble in ether than its lower homologue, and, as seen from the fact that it was also obtained from the previously-described extract of the resin, it is very slightly soluble in petroleum, whilst olestranol appears to be insoluble in this solvent. With the exception of these slight differences, the two homologous hydroxyphytosterols could only be distinguished by their melting points or by analysis, as their behaviour on acetylation, benzoylation, and bromination is identical. Homo-olestranol does not yield the colour reaction characteristic of the so-called "oxycholesterin" of Lifschütz (*Ber.*, 1908, **41**, 252), which, however, does not appear to have been analysed.

A determination of the specific rotatory power of homo-olestranol yielded the following result:

0·7216, dissolved in 25 c.c. of chloroform, gave a_D + 4°6′ in a 2-dcm. tube, whence $[a]_D$ + 71·0°.

The amount of olestranol available did not permit of a similar determination being made with that compound.

Chloroform, Ethyl Acetate, and Alcohol Extracts of the Resin.

The chloroform extract of the resin amounted to 9 grams. It was exhaustively examined, but nothing crystalline could be obtained from it.

The portion of the resin extracted by ethyl acetate amounted to only 2 grams. It consisted of tarry matter, together with a trace of *d*-mannitol, which was subsequently isolated in larger amount from the aqueous liquid.

The remainder of the resin, which was soluble only in alcohol, formed a brown powder, and amounted to 23 grams. Nothing crystalline could be separated from it, and, in view of the possibility of its containing some glucosidic material, it was freed from any traces of sugar and submitted to the action of sulphuric acid in dilute alcohol, but was unaltered by this treatment.

Examination of the Brown Resin (*B*).

This product, obtained as previously described, amounted to 47 grams. It was mixed with purified sawdust, and extracted with the same solvents as were employed in the case of the green resin. The petroleum and ethereal extracts thus obtained were small in amount, and consisted chiefly of the material which formed the corresponding extracts from the resin previously examined. The remaining extracts, of which that obtained by ethyl acetate was the largest, were all brown, resinous products, from which nothing crystalline could be isolated.

Examination of the Aqueous Liquid (*C*).

After concentrating this liquid, it was extracted many times with ether, but this removed only a small amount of amorphous material, containing but a trace of crystalline substance. An excess of a solution of basic lead acetate was then added, when a bulky, yellow precipitate was produced, which was removed by filtration and thoroughly washed with boiling water. This precipitate was suspended in water, decomposed by hydrogen sulphide, and the mixture filtered. The filtrate was concentrated and allowed to cool, when a quantity of brown, viscid, resinous matter separated. The clear liquid was then extracted with amyl alcohol, when a further quantity of brown, viscid material was removed. These resinous products possessed a bitter, astringent taste, and, when dissolved in boiling water, readily reduced Fehling's solution, but nothing crystalline could be obtained from them. The brown, aqueous liquid which had been extracted with amyl alcohol gave a deep black colour with ferric chloride, and evidently contained a considerable amount of tannin. When treated with a solution of barium hydroxide, it gave a yellow precipitate, which rapidly darkened in the air, but nothing could be isolated from it.

The original aqueous filtrate and washings from the precipitate produced by basic lead acetate were freed from a further small quantity of brown material by a second treatment with this reagent then deprived of lead by means of hydrogen sulphide, again filtered, and concentrated under diminished pressure. On allowing the liquid to stand, it deposited a large amount (60 grams) of needle-shaped crystals, which, after recrystallisation from dilute alcohol, melted at 165°:

0·1183 gave 0·1717 CO_2 and 0·0830 H_2O. $C = 39{\cdot}6$; $H = 7{\cdot}8$.

$C_6H_{14}O_6$ requires $C = 39{\cdot}6$; $H = 7{\cdot}7$ per cent.

This substance was evidently *d*-mannitol, since it yielded a dextrorotatory hexa-acetyl derivative, which melted at 122—123°.

The filtrate from the crude mannitol deposited further quantities of the latter on concentration, but no other solid substance could be separated from it. It contained a considerable amount of sugar, for, when warmed with a solution of phenylhydrazine acetate, it readily yielded *d*-phenylglucosazone, which, when heated somewhat rapidly, melted at 217°. In view of the possibility of this final aqueous liquid also containing a glucoside, it was heated for some time with dilute sulphuric acid, but this treatment resulted only in the production of a quantity of resin, together with a little furfural.

Summary.

The results of this investigation may be summarised as follows:

The air-dried olive leaves employed, on percolation with boiling alcohol, yielded about 30 per cent. of their weight of extracted material, of which nearly 63 per cent. was soluble in cold water. A further 8·7 per cent. could be dissolved by boiling water, whilst the remainder, amounting to 28·3 per cent., was quite insoluble in this solvent. The alcoholic extract, when distilled with steam, yielded a trace of essential oil.

The portion of the alcoholic extract which was soluble in cold water contained a large quantity of a sugar which yielded *d*-phenylglucosazone

(m. p. 217°), together with tannic matter, brown, amorphous products, and an amount of *d*-mannitol equivalent to about 3·4 per cent. of the weight of the air-dried leaves.

The portion of the alcoholic extract which was dissolved by boiling water, but separated on cooling, consisted of amorphous resins.

The material insoluble in water contained, together with chlorophyll and some resinous matter, small amounts of the hydrocarbons hentriacontane, $C_{31}H_{64}$ (m. p. 68—69°), and pentatriacontane, $C_{35}H_{72}$ (m. p. 74·5°), a little of a mixture of fatty acids, and a new *monocarboxylic acid*, $C_{22}H_{45}\cdot CO_2H$ (m. p. 68—69°). In addition to these, it yielded three new crystalline alcohols, which appear to be related to the phytosterols, namely, *oleasterol*, $C_{20}H_{34}O$ (m. p. 174°), which crystallises in tufts of colourless needles; *olestranol*, $C_{25}H_{42}O_2$ (m. p. 217—218°), and *homo-olestranol*, $C_{27}H_{46}O_2$ (m. p. 210°; $[\alpha]_D$ +71°). The two last-mentioned alcohols crystallise in hard, wart-like masses, and appear to be *hydroxyphytosterols*. Furthermore, a new colourless, crystalline substance, *oleanol*, $C_{31}H_{48}O(OH)_2,H_2O$ m. p. 303—304°; $[\alpha]_D^{20}$ +78·3°), was obtained in an amount equivalent to nearly 3·4 per cent. of the weight of the air-dried leaves. Oleanol contains two hydroxyl groups, one of which possesses phenolic properties. When treated with sodium ethoxide and methyl iodide, it yields a *monomethyloleanol*, $C_{31}H_{48}O(OH)\cdot O\cdot CH_3$ (m. p. 194—195°), and this, on acetylation, gives *acetylmethyloleanol*,

$$C_{31}H_{48}O_2(O\cdot CH_3)\cdot CO\cdot CH_3$$

(m. p. 215·5°). *Diacetyloleanol*, $C_{31}H_{48}O_3(CO\cdot CH_3)_2$, fuses at about 208°, and suffers a change which is accompanied by the evolution of gas and the formation of a crystalline *substance*, $C_{31}H_{48}O_3$, which does not melt at 310°. *Monoacetyloleanol*, $C_{31}H_{48}O_2(OH)\cdot CO\cdot CH_3$ (m. p. 258°), was prepared by heating the diacetyl derivative with aqueous alcohol.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

LXXXIV.—*The Constituents of Olive Bark.*

By FREDERICK BELDING POWER and FRANK TUTIN.

THE bark of the olive tree, *Olea Europaea*, Linné, is reputed to possess medicinal properties similar to those of the leaves, but, with the exception of the observation that, like other parts of the plant, it contains mannitol, nothing appears to have been ascertained respecting the character of its constituents. It may be noted, however, that from a so-called gum-resin, which excludes spontaneously from the bark of the olive tree in hot countries, a crystalline substance, designated olivil, was isolated many years ago. This substance which, as our investigation has shown, does not occur in the bark, has most recently been examined by Körner and Vanzetti (*Atti R. Accad. Lincei*, 1903, [v], **12**, i, 122), who state that, when anhydrous, it possesses the formula $C_{20}H_{24}O_7$ and melts at 142·5°.

In connexion with our investigation of olive leaves, it has been deemed desirable also to examine the constituents of the bark of the olive tree, and the results obtained are recorded in this communication.

EXPERIMENTAL.

The material employed in this investigation consisted of the air-dried bark of *Olea Europaea*, Linné, which had been collected for us during the early spring in the neighbourhood of Ventimiglia, on the Italian Riviera.

A portion of the bark was first tested for the presence of an alkaloid, but with a negative result.

Fifty grams of the ground bark were then successively extracted in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried at 100°, were obtained:

Petroleum (b. p. 35—50°)	extracted	0·32	per cent.
Ether	,,	3·76	,,
Chloroform	,,	6·30	,,
Ethyl acetate	,,	4·56	,,
Alcohol	,,	15·30	,,
	Total	30·24	,,

For the purpose of a complete examination, a quantity (34·92 kilograms) of the ground bark was extracted by continuous percolation with hot alcohol. One kilogram of the resulting viscous extract, containing 875 grams of extracted material, was then mixed with water and distilled with steam, but no volatile product was obtained. The dark-coloured, aqueous liquid in the distillation flask was separated by filtration, while still hot, from a relatively small amount of dark green resin (*A*), and the latter thoroughly washed with boiling water. The combined filtrate and washings were then diluted to about 10 litres and allowed to cool, when a large amount of a heavy, brown, syrupy product (*B*) was deposited. This was separated, and freed from substances soluble in cold water, after which the combined aqueous liquid and washings (*C*) were concentrated to about 2 litres.

Examination of the Green Resin (A).

This resin, which amounted to 54 grams, was a dark green, wax-like solid at the ordinary temperature, but when heated to about 80° it melted to an oil. After being mixed with purified sawdust, it was successively extracted in a Soxhlet apparatus with the following solvents: petroleum (b. p. 35—50°), ether, chloroform, ethyl acetate, and alcohol.

Petroleum Extract of the Resin.

Isolation of a New Monocarboxylic Acid, $C_{34}H_{67}\cdot CO_2H$.

The petroleum extract of the resin was a dark green, wax-like solid, and weighed 28·6 grams. It was dissolved in ether, and the ethereal liquid shaken with a solution of sodium carbonate, when a quantity of a green, flocculent precipitate was formed. The ethereal and aqueous liquids were separated from the precipitate by filtration, when, on acidifying the latter liquid, it was found to contain no insoluble acid. The solid was then well washed with ether, warmed with dilute sulphuric acid, and the liberated acid isolated by means of chloroform. On removing the solvent, a green residue was obtained, which was distilled under diminished pressure. The light brown distillate solidified on cooling, and was crystallised from ethyl acetate, with the use of animal charcoal. Small, colourless leaflets were thus obtained which melted at 69—70°, and this melting point was not altered by repeated crystallisation. Two different preparations of this substance were analysed:

0·1036 gave 0·3071 CO_2 and 0·1242 H_2O. C = 80·5; H = 13·3.
0·1033 „ 0·3049 CO_2 „ 0·1246 H_2O. C = 80·5; H = 13·4.
$C_{35}H_{68}O_2$ requires C = 80·8; H = 13·1 per cent.

This *acid* would thus appear to possess the formula $C_{35}H_{68}O_2$, and, since no substance of this formula has previously been described, it is apparently a new compound. It behaves towards bromine as a saturated compound, and yields *sodium*, *potassium*, and *ammonium* salts, which are insoluble in water. It is only sparingly soluble in cold chloroform or in boiling alcohol, and a warm solution of it in the former solvent was found to be optically inactive. It was not possible to titrate accurately this acid, or any of the analogous acids subsequently described, on account of their sparing solubility and the flocculent character of their insoluble salts.

The *ethyl* ester was prepared by means of ethyl alcohol and sulphuric acid. After being freed from traces of unchanged acid, it crystallised in leaflets melting at 63°:

0·1140 gave 0·3386 CO_2 and 0·1390 H_2O. C = 81·0; H = 13·5.
$C_{34}H_{67}\cdot CO_2\cdot C_2H_5$ requires C = 81·0; H = 13·1 per cent.

Isolation of a New Monocarboxylic Acid, $C_{24}H_{45}\cdot CO_2H$.

The green, ethereal liquid, from which the above-described acid had been removed by means of sodium carbonate, was shaken with a solution of sodium hydroxide. This treatment caused the separation of a precipitate similar to that previously produced by sodium carbonate, but the amount was somewhat larger. The alkaline, aqueous liquid obtained in this case also yielded nothing on acidification. The precipitate apparently consisted of a sodium derivative. It was therefore warmed with dilute sulphuric acid, and the mixture extracted with chloroform, when, on evaporating the chloroformic liquid, a green, wax-like solid was obtained. This was crystallised from ethyl acetate, with the use of animal charcoal, when it separated in small, colourless leaflets, which melted at 79°, and this melting-point was not altered by further crystallisation.

0·1175 gave 0·3406 CO_2 and 0·1304 H_2O. C = 79·1 ; H = 12·3.
0·1106 „ 0·3216 CO_2 „ 0·1236 H_2O. C = 79·3 ; H = 12·4.
$C_{25}H_{46}O_2$ requires C = 79·3 ; H = 12·2 per cent.

Notwithstanding the fact that this substance cannot be removed from its solution in ether by means of sodium carbonate, a property which was confirmed when working up a second portion of extract from the bark, it must be regarded as a carboxylic acid, for it crystallises unchanged from acetic anhydride after being boiled for some time with this reagent, exhibits an acid reaction to phenolphthalein, and yields an ethyl ester. Since no compound of the formula $C_{25}H_{46}O_2$ has hitherto been described, it must, moreover, be regarded as a new *acid*. It is very sparingly soluble in alcohol, behaves towards bromine as a saturated substance, and, when dissolved in chloroform, is optically inactive.

The *ethyl* ester was prepared in the usual manner by means of ethyl alcohol and sulphuric acid. It was dissolved in chloroform, and freed from unchanged acid by means of sodium hydroxide, after which it was crystallised from ethyl acetate, when it separated in glistening plates melting at 66·5°:

0·0946 gave 0·2775 CO_2 and 0·1060 H_2O. C = 80·0 ; H = 12·4.
$C_{24}H_{45}\cdot CO_2\cdot C_2H_5$ requires C = 79·8 ; H = 12·3 per cent.

Isolation of Ipuranol, $C_{23}H_{38}O_2(OH)_2$.

The original ethereal liquid, which had been shaken with solutions of sodium carbonate and hydroxide, was washed with water, when a deep green, alkaline, aqueous liquid was obtained, which evidently contained a large amount of chlorophyll in combination with sodium. This solution was acidified with sulphuric acid, when the chlorophyll was precipitated. On attempting to extract the latter with ether, a quantity of solid remained undissolved, and was collected on a filter. This solid was washed by boiling it with several successive portions of ether, and then dissolved in boiling alcohol, in which it was very sparingly soluble. The alcoholic solution, which was green, was decolorised by means of animal charcoal, when, on allowing it to cool, a small quantity (less than 0·1 gram) of a colourless solid separated in the form of small, very flocculent tufts of extremely fine needles. This substance was not very distinctly crystalline, but was obtained more definitely so on cooling its solution in dilute pyridine. In order to obtain it in greater amount, a further large quantity of extract from the bark was employed. The substance, even when pure, does not melt sharply, but fusion takes place between 285° and 290°, some gas being evolved from the melted substance.

0·0944 gave 0·2510 CO_2 and 0·0907 H_2O. C = 72·6 ; H = 10·7.
0·1034 „ 0·2752 CO_2 „ 0·0984 H_2O. C = 72·6 ; H = 10·6.
$C_{23}H_{40}O_4$ requires C = 72·6 ; H = 10·5 per cent.

Although no compound of the formula $C_{23}H_{40}O_4$ has hitherto been brought to notice, a substance having this composition was recently isolated in small amount in these laboratories from the stems of *Ipomoea purpurea*, Roth (*Amer. J. Pharm.*, in the press), and the two preparations have been found to be identical. This substance, with reference to the source from which it first was obtained, has received the designation *ipuranol*.

Diacetylipuranol, $C_{23}H_{38}O_4(CO{\cdot}CH_3)_2$.—A small quantity of ipuranol was boiled with acetic anhydride, when it very slowly dissolved. On concentrating the solution and allowing it to cool, ***diacetylipuranol*** separated in well-defined, glistening leaflets, which melted at 160°:

0·1124 gave 0·2875 CO_2 and 0·0949 H_2O. C = 69·8 ; H = 9·4.
$C_{23}H_{38}O_4(CO{\cdot}CH_3)_2$ requires C = 69·8 ; H = 9·5 per cent.

The identity of the substance, $C_{23}H_{40}O_4$, from olive bark with ipuranol (from *Ipomoea purpurea*) was further confirmed by a comparison of their respective acetyl derivatives. Since ipuranol yields a diacetyl derivative, it evidently contains two hydroxyl groups, and, inasmuch as it gives a sodium derivative when treated with sodium hydroxide, one at least of these groups must possess phenolic properties. Diacetylipuranol, however, when dissolved in chloroform, does not react with aqueous alkalis.

Ipuranol is quite insoluble in petroleum, and nearly so in ether. It could not therefore have been present in the petroleum extract of the resin in a free state, and, as it was obtained from the chlorophyll after the latter had been removed from the ethereal solution of the petroleum extract in the form of a compound with the alkali, it probably existed in the bark in combination with some constituent of the chlorophyll which suffered hydrolysis whilst in solution in the dilute aqueous sodium hydroxide.

The original ethereal liquid from which the ipuranol had been obtained was evaporated, and the residue boiled for some time with an alcoholic solution of an excess of potassium hydroxide. The alcohol was then removed, water added, and the liquid extracted with ether. A small quantity of a flocculent precipitate collected in the lower portion of the ethereal layer, which was found to consist of an insoluble potassium salt. The acid obtained from this salt crystallised from ethyl acetate in plates melting at 67°, but the amount was not sufficient for analysis. The alkaline aqueous liquid was separated and found to contain, besides formic and butyric acids in small amount, only chlorophyll and amorphous matter. The ethereal solution of the unsaponifiable substances was bright yellow. The solvent was removed, and the residue fractionally crystallised from absolute alcohol, when a very small amount of a substance was obtained, which, after distillation under diminished pressure, crystallised in small plates melting at 74—75°:

0·0804 gave 0·2503 CO_2 and 0·1071 H_2O. C = 84·9 ; H = 14·8.

$C_{35}H_{72}$ requires C = 85·4 ; H = 14·6 per cent.

This substance was thus identified as pentatriacontane.

The mother liquors from this hydrocarbon yielded a substance which, after several recrystallisations, separated from a mixture of ethyl acetate and dilute alcohol in long, flattened needles, which melted at 134°. After being distilled under diminished pressure, and again crystallised as before, the substance melted at 136°:

0·1076, on drying at 110°, lost 0·0053 H_2O. H_2O = 4·9.

0·0917 gave 0·2804 CO_2 and 0·1008 H_2O. C = 83·4 ; H = 12·2.

$C_{27}H_{46}O,H_2O$ requires H_2O = 4·5.

$C_{27}H_{46}O$ requires C = 83·9 ; H = 11·9 per cent.

The substance therefore was evidently a phytosterol, and, when dissolved in chloroform and treated with acetic anhydride and sulphuric acid, it yielded the colour reaction characteristic of these alcohols. It differed, however, in appearance from the phytosterols usually obtained, since it crystallised in long, flattened needles, and not in plates. A determination of its optical rotatory power gave the following result:

0·3965 of anhydrous substance, dissolved in 25 c.c. of chloroform gave $[\alpha]_D$ − 1°7′ in a 2-dcm. tube, whence $[\alpha]_D$ − 35·2°.

The melting point and rotation of this phytosterol agree approximately with those of sitosterol (*Zeitsch. physiol. Chem.*, 1902, **34**, 461), which melts at 137° and has $[\alpha]_D$ − 33·9°. The acetate of the phytosterol from olive bark, however, crystallised in silky laminæ melting at 119·5°, and this melting point could not be raised, whereas sitosteryl acetate melts at 128°. It would appear therefore that the two alcohols are not identical.

Ethereal Extract of the Resin.

Isolation of a New Monocarboxylic Acid, $C_{34}H_{69}\cdot CO_2H$.

The portion of the resin removed by ether amounted to 13 grams. As originally obtained, it consisted of a green, ethereal solution containing a quantity (about 4 grams) of a light-coloured precipitate. The latter was collected on a filter and well washed with ether, after which it was dissolved in a large volume of hot alcohol, the solution decolorised by means of animal charcoal, and allowed to cool. A quantity of a white, amorphous solid then separated. This was collected on a filter, again dissolved in hot alcohol, and allowed to separate, but it still remained amorphous. The solid substance, which melted at 90°, was therefore dried and then distilled under a pressure of 13 mm., when it passed over up to 365° without decomposition. The distillate was crystallised from ethyl acetate, from which it separated in small, colourless leaflets melting at 92°:

0·0975 gave 0·2872 CO_2 and 0·1189 H_2O. C = 80·3; H = 13·5.
0·0855 „ 0·2524 CO_2 „ 0·1043 H_2O. C = 80·5; H = 13·5.
$C_{35}H_{70}O_2$ requires C = 80·5; H = 13·4 per cent.

This substance was an *acid*, as was evident from its behaviour to phenolphthalein. It yields *sodium*, *potassium*, and *ammonium* salts, which are flocculent, insoluble solids, and readily gives an *ethyl* ester. Since no substance of the formula $C_{35}H_{70}O_2$ has heretofore been described, it must, moreover, be regarded as a new compound. The acid is only sparingly soluble in most of the usual organic solvents when cold, and, so far as could be observed with a dilute chloroformic liquid, it is optically inactive. It would not appear probable, however, that it is a normal fatty acid, since it is absolutely insoluble in light petroleum. It is also more soluble in boiling alcohol than the acid $C_{35}H_{68}O_2$, which was obtained from the petroleum extract of the resin.

A small quantity of the *ethyl* ester was prepared. This crystallised in leaflets, which were rather larger than those of the corresponding acid, and melted at 87°.

Isolation of a New Monohydric Alcohol, $C_{35}H_{67}\cdot OH$.

The above described acid, melting at 92°, did not represent the whole of that portion of the ethereal extract of the resin which was sparingly soluble in this solvent. It was evident that a mixture of other substances of lower melting point was present in the mother liquors together with a trace of a compound melting above 250°, which will be referred to later. A further and much larger quantity of the sparingly soluble material was obtained, and submitted to fractional distillation under diminished pressure, when the following fractions were collected: below 250°, 250—290°, 290—320°, 320—360°/13 mm. The last two fractions, on crystallisation, yielded a product which melted at 87°, and, on analysis, was found to consist essentially of the above-described acid (m. p. 92°). The portion boiling below 250° was only small in amount and was not examined, but the fraction 250—290°/13 mm. yielded a product which crystallised from ethyl acetate in flattened needles melting at 70°, and this melting point was not altered by repeated crystallisation. On analysis, it gave the following result:

0·0907 gave 0·2778 CO_2 and 0·1136 H_2O. C = 83·5; H = 13·9.
$C_{35}H_{68}O$ requires C = 83·3; H = 13·5 per cent.

This *substance* is evidently identical with the compound, melting at the same temperature, which was subsequently isolated from the portion of the ethereal extract of the resin which was more readily soluble in this solvent, although the percentage of carbon found is a trifle too high. It may be noted that its formula differs by the elements of one molecule of water from that of the above-described acid melting at 92°, but it is much more soluble than the latter in chloroform.

The boiling point of the fraction, from which this substance was obtained, shows that the molecular weight of the compound cannot be twice that indicated by the above formula. The substance therefore contains only one oxygen atom, but, notwithstanding this fact, it can be removed completely from its solution in chloroform or benzene by means of sodium hydroxide, an insoluble, flocculent *sodium* compound being formed. The slight phenolic properties of the compound may be accounted for by regarding it as a tertiary alcohol and by its possessing such a high molecular weight. An acetyl derivative could not be obtained from it, and this also indicated that it did not contain a primary or secondary alcoholic grouping. Since no compound of the formula $C_{35}H_{68}O$ has previously been described, it must, moreover, be regarded as a new substance. When dissolved in chloroform, it does not absorb bromine, and would therefore appear to possess a cyclic structure.

The original alcoholic mother liquors, obtained after the preliminary purification by means of animal charcoal, of that portion of the ethereal extract of the resin which was sparingly soluble in this solvent contained, as previously stated, a very small amount of a substance melting above 250°. They were therefore evaporated to dryness, and the residue extracted with boiling benzene. The small amount of material which remained undissolved by this treatment was crystallised from dilute pyridine, after which it melted at 285—290°, and by conversion into its acetyl derivative (m. p. 160°) was identified as ipuranol. This trace of ipuranol, obtained from the ethereal extract of the resin, had evidently existed in the plant in the free state.

Isolation of a New Monocarboxylic Acid, $C_{29}H_{57}\cdot CO_2H$.

The original ethereal filtrate from the sparingly soluble precipitate, the examination of which has just been described, was shaken with a solution of ammonium carbonate. This caused the separation of a flocculent *ammonium* salt, which was collected on a filter and well washed with ether. The aqueous portion of the filtrate from this precipitate yielded nothing on acidification. The precipitate was treated with dilute sulphuric acid, and the liberated acid extracted by means of chloroform. On removing the solvent, a green, wax-like solid was obtained, which was distilled under diminished pressure, after which it was crystallised from ethyl acetate with the use of animal charcoal. The acid then separated in small, glistening leaflets melting at 82°, and when again crystallised from ethyl acetate its melting point was raised to 84°:

0·0938 gave 0·2748 CO_2 and 0·1104 H_2O. C = 79·9; H = 13·1.

After another crystallisation, the melting point of the substance remained unchanged, and it was again analysed:

0·0950 gave 0·2784 CO_2 and 0·1103 H_2O. C = 79·9; H = 12·9.

$C_{30}H_{58}O_2$ requires C = 80·0; H = 12·9 per cent.

As no compound possessing the formula $C_{30}H_{58}O_2$ has previously been described, the substance melting at 84° must be regarded as a new *monocarboxylic acid*. Its empirical formula would appear to indicate that it belongs to the oleic acid series, but, when dissolved in chloroform, it does not absorb bromine, and may therefore be considered to possess a cyclic structure.

The *ethyl* ester of this acid was prepared in the usual manner, and, after being freed from traces of unchanged acid, was found to melt at 75°. It crystallised from ethyl acetate in glistening plates, which dried to a parchment-like mat:

0·0939 gave 0·2766 CO_2 and 0·1114 H_2O. C = 80·3; H = 13·2.

$C_{29}H_{57}\cdot CO\cdot C_2H_5$ requires C = 80·3; H = 13·0 per cent.

The ethereal liquid, from which the above-described acid had been obtained in the form of its ammonium salt, was shaken with a solution of sodium carbonate. Nothing was dissolved by this alkali, but a small amount of a flocculent precipitate separated, from which, however, no pure substance could be isolated.

The ethereal liquid was then shaken with a solution of sodium hydroxide, when a flocculent, insoluble sodium compound separated. The latter was treated with dilute sulphuric acid, and the liberated substance extracted by means of chloroform. On removing the solvent, a residue was obtained which contained a considerable amount of chlorophyll. It was purified by several distillations under diminished pressure, and finally by crystallisation from ethyl acetate, when colourless, flattened needles, melting at 70°, were eventually obtained:

0·0847 gave 0·2583 CO_2 and 0·1061 H_2O. $C=83{\cdot}2$; $H=13{\cdot}9$.
0·0984 „ 0·3003 CO_2 „ 0·1212 H_2O. $C=83{\cdot}2$; $H=13{\cdot}7$.
$C_{35}H_{68}O$ requires $C=83{\cdot}3$; $H=13{\cdot}5$ per cent.

This compound was identical with the previously-described substance of the same composition and melting point, which is probably a tertiary alcohol.

The final ethereal solution, which had been extracted by alkalis as above described, contained only a trace of amorphous, green substance.

Chloroform, Ethyl Acetate, and Alcohol Extracts of the Resin.

The chloroform extract of the resin amounted to about 6 grams, and was evidently a complex mixture. It was shaken with aqueous alkalis, but no pure substance could be obtained from it.

The portion of material removed by ethyl acetate was very small. It consisted of resin together with a trace of *d*-mannitol, which had escaped extraction by water during the preliminary treatment.

The remaining small portion of the resin, which was soluble only in alcohol, consisted of a brown, amorphous product.

Examination of the Brown Resin (B).

This product, as first obtained, was a heavy, brown, viscid syrup. After being completely freed from substances soluble in cold water, it was dried on a water-bath, when it formed a somewhat soft, brown resin, amounting to 283 grams. This was dissolved in alcohol, and the solution evaporated on purified sawdust, after which the dry material was extracted successively in a large Soxhlet apparatus with ether, chloroform, ethyl acetate, and alcohol.

The amount of material removed by ether was very small. It was freed from a trace of substance soluble in petroleum, redissolved in ether, and then extracted with a solution of ammonium carbonate.

The aqueous, alkaline liquid thus obtained, after filtering, was acidified with sulphuric acid, a small quantity of precipitated tarry matter removed, and the solution then extracted many times with ether. The ethereal liquid, on evaporation, yielded a small, crystalline residue, which, after recrystallisation from alcohol, melted at 265°, and was identical with a compound which was subsequently obtained in larger amount from the aqueous liquid (*C*). No other crystalline substance could be obtained from the ethereal extract of the brown resin.

The chloroform extract of the brown resin was relatively small in amount, and, although exhaustively examined, it yielded nothing crystalline.

The ethyl acetate extract represented the greater part of the brown resin, but nothing could be separated from it. A large proportion of it was only sparingly soluble in ethyl acetate, and, in view of the possibility of this containing a glucosidic substance, it was freed from any traces of sugar and then heated with dilute alcoholic sulphuric acid. On evaporating the alcohol after this treatment, a quantity of a black resin was obtained, from which nothing could be isolated, but, after removing the sulphuric acid from the aqueous liquid, the latter yielded a small quantity of *d*-phenylglucosazone. It was thus evident that some material of a glucosidic nature was present in the ethyl acetate extract.

The remaining portion of the brown resin, which was soluble only in alcohol, amounted to about one-third of the whole. Its solution in alcohol dried to a hard, brown varnish. When treated with dilute alcoholic sulphuric acid, it yielded a quantity of dextrose, but the only other product was an amorphous resin.

Examination of the Aqueous Liquid (*C*).

Isolation of a New Phenolic Substance, Olenitol, $C_{14}H_{10}O_6$.

The concentrated aqueous liquid (*C*) was repeatedly extracted with ether, the combined ethereal liquids shaken with several successive portions of a solution of sodium carbonate, and the alkaline liquids then separately examined. The liquid obtained by the first extraction with sodium carbonate yielded, on acidification, a precipitate of a dark brown, heavy oil, and, when allowed to stand for some time, it also deposited a small amount of pale yellow crystals. The mixture was shaken with a small volume of ether, when apparently only the oil dissolved, and the crystals were then collected on a filter. The ethereal portion of the filtrate was then separated, but this was found to contain only a brown, oily product. A further small quantity of the crystalline substance was, however, obtained by repeatedly extracting the acid, aqueous liquid with ether.

The liquid obtained by shaking the ethereal extract of the aqueous liquid with a second portion of sodium carbonate solution also yielded a small amount of this crystalline substance, but all the subsequent extractions with this alkali gave only tarry products. The original ethereal liquid, after complete extraction with sodium carbonate, yielded only a brown, viscid syrup.

The different portions of the crystalline substance were mixed and recrystallised from alcohol, when it was obtained in short, yellow needles melting at about 265°. This product was found to be identical with the small amount of crystalline substance which had been obtained from the ethereal extract of the brown resin, as already described. The products from the two sources were therefore mixed and again crystallised from alcohol, after which the substance still melted at about 265°, although not quite sharply, some decomposition occurring. On drying at 110°, it was found to be anhydrous:

0·0988 gave 0·2220 CO_2 and 0·0338 H_2O. $C = 61 \cdot 3$; $H = 3 \cdot 8$.

As the amount of this substance available was not sufficient for another analysis, a further portion of it was obtained by working up a larger quantity of the original extract of the bark, and this, on analysis, gave the following result:

0·0988 gave 0·2216 CO_2 and 0·0327 H_2O. $C = 61 \cdot 2$; $H = 3 \cdot 7$.

$C_{14}H_{10}O_6$ requires $C = 61 \cdot 3$; $H = 3 \cdot 6$ per cent.

The properties of this substance do not agree exactly with those of any compound of the formula $C_{14}H_{10}O_6$ which has previously been described. It was thought, however, that it might possibly be identical with a substance prepared by A. Michael (*J. pr. Chem.*, 1887, [ii], **35**, 510) by the condensation of ethyl oxalate with resorcinol, which is stated to fuse at about 259°. A quantity of the latter substance was therefore prepared, but was found to differ totally in many of its properties from the compound from olive bark. The yellow, crystalline substance $C_{14}H_{10}O_6$ is therefore a new compound, and it is proposed to designate it *olenitol.*

Olenitol is slightly soluble in water, ether, or ethyl acetate, and somewhat more readily so in alcohol. Its dilute solution in water or aqueous alcohol is slightly yellow, and exhibits a pale blue fluorescence. When dissolved in cold sulphuric acid, olenitol gives a colourless solution, but its solution in alkalis is intensely yellow, and, when largely diluted, displays a violet-blue fluorescence. An aqueous solution of olenitol gives with ferric chloride an intense, moss-green colour.

Olenitol does not contain a carboxyl group, since its acetyl derivative is insoluble in cold aqueous alkalis. It must, therefore, be regarded as a phenolic compound. Methoxyl groups also do not appear to be present, for the olenitol was recovered unchanged after being boiled for an hour with 70 per cent. sulphuric acid.

Acetylolenitol was prepared by boiling olenitol with acetic anhydride for half an hour. The anhydride was then decomposed by water, and the greater part of the acetic acid neutralised by sodium carbonate. Acetylolenitol then separated in a crystalline form, and, after recrystallisation from alcohol, was obtained in nearly colourless leaflets, melting at 130°. The amount of this derivative was, however, not sufficient for analysis.

The original aqueous liquid, which had repeatedly been extracted with ether, was shaken with many successive portions of amyl alcohol. This treatment removed about 80 grams of a product which was similar in appearance to the previously-described brown resin (*B*). It was exhaustively examined, and found to be a very complex mixture. All the products obtained from it were brown, very viscid syrups, which, when dissolved in boiling water, reduced Fehling's solution, but nothing crystalline could be obtained from them.

The aqueous liquid, after being freed from amyl alcohol by means of steam, was treated with an excess of a solution of basic lead acetate. A bulky, yellow precipitate was thus obtained, which was collected on a filter, well washed with boiling water, then suspended in water, and decomposed by hydrogen sulphide. The liquid filtered from the lead sulphide, when concentrated, formed a brown syrup, which appeared to contain a large amount of tannic matter, but the only crystalline substance that could be isolated from it was a trace of oxalic acid.

The filtrate from the basic lead acetate precipitate was deprived of lead, and concentrated under diminished pressure, when, on allowing it to stand for some time, it deposited a quantity (55 grams) of crystals. These were collected and recrystallised from dilute alcohol, after which they melted at 165° and were identified as *d*-mannitol:

0·1035 gave 0·1505 CO_2 and 0·0750 H_2O. $C = 39·7$; $H = 8·0$.

$C_6H_{14}O_6$ requires $C = 39·6$; $H = 7·7$ per cent.

The original syrupy filtrate from the *d*-mannitol readily reduced Fehling's solution, and evidently contained a large amount of sugar, for, when warmed with phenylhydrazine acetate, it yielded *d*-phenylglucosazone, which, when heated somewhat rapidly, melted at 217°.

The liquid was further tested for the presence of a glucoside, but only a black resin and a little furfuraldehyde were obtained.

Summary.

The results of this investigation may be summarised as follows:

The air-dried olive bark employed, on percolation with hot alcohol, yielded about 30 per cent. of its weight of extracted material, of which

61·5 per cent. was soluble in cold water. A further 32·3 per cent. could be dissolved by boiling water, but separated on cooling, whilst the remainder amounting to about 6·2 per cent., was quite insoluble in either cold or hot water.

The portion of the alcoholic extract which was dissolved by cold water contained an amount of *d*-mannitol equivalent to nearly 1·9 per cent. of the weight of air-dried bark, together with tannic matter, viscid, brown products, and a sugar which yields *d*-phenylglucosazone. It also contained a small amount of a new, crystalline phenolic substance, *olenitol*, $C_{14}H_{10}O_6$ (m. p. 265°), dilute solutions of which show a blue fluorescence. *Acetylolenitol* melts at 130°.

The portion of the alcoholic extract which was soluble in hot but not in cold water consisted for the most part of brown, resinous products, some of which yielded glucose on hydrolysis, but a small amount of olenitol was also obtained from them.

The material insoluble in water consisted chiefly of a mixture of new *monocarboxylic acids*, all of which crystallise from ethyl acetate in small leaflets. They have the following composition and properties: (1) an *acid*, $C_{34}H_{67}\cdot CO_2H$ (m. p. 69—70°), which yields an *ethyl* ester melting at 63°; (2) an *acid*, $C_{24}H_{45}\cdot CO_2H$ (m. p. 79°), the *ethyl* ester of which melts at 66·5°. Both of these acids are soluble in petroleum (b. p. 35 – 50°); (3) an *acid*, $C_{34}H_{69}\cdot CO_2H$ (m. p. 92°), which is insoluble in petroleum, and yields an *ethyl* ester melting at 87°; (4) an *acid*, $C_{29}H_{57}\cdot CO_2H$ (m. p. 84°), which yields an *ethyl* ester melting at 75°, and, like the preceding one, is insoluble in light petroleum. In addition to these acids, a *substance*, probably a *tertiary alcohol*, $C_{35}H_{68}O$ (m. p. 70°), was obtained, together with a small amount of pentatriacontane, $C_{35}H_{72}$ (m. p. 74—75°), a phytosterol, $C_{27}H_{46}O$ (m. p. 136°; $[\alpha]_D - 35\cdot2°$), the acetate of which melts at 119·5°, and a very small amount of a *substance*, $C_{23}H_{38}O_2(OH)_2$ (m. p. 285—290°), which yields an *acetyl* derivative, $C_{23}H_{38}O_4(CO\cdot CH_3)_2$, melting at 160°. This last-mentioned substance is identical with a compound which has recently been isolated by Power and Rogerson from *Ipomoea purpurea*, and designated *ipuranol*.

In conclusion it may be noted that the constituents of olive bark are quite dissimilar to those of the leaves, as our investigations have shown that only three substances are common to both, namely, *d*-mannitol, sugar, and pentatriacontane. In view of the large percentage of fatty oil contained in the ripe fruit of the olive tree, it may also be considered remarkable that the bark should be devoid of even traces of the ordinary fatty acids.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

LXXXV.—*The Refraction and Dispersion of Triazo-compounds.*

By JAMES CHARLES PHILIP.

THE spectrochemistry of nitrogen has been made the subject of exhaustive investigation by Brühl (*Zeitsch. physikal. Chem.*, 1894, **16**, 193, 226, 497, 512; 1897, **22**, 373; 1898, **25**, 577; **26**, 47), and from his researches it appears that the contribution which the nitrogen atom makes to the molecular refraction or dispersion of a compound depends very markedly on the character and arrangement of the other atoms or groups with which the nitrogen is linked. This result obviously suggests that the determination of the optical constants of a compound containing nitrogen may be useful in throwing light on its constitution, and Brühl himself has made frequent use of refraction and dispersion for this purpose.

It has been found possible to add a little to our knowledge of the spectrochemistry of nitrogen by a study of the interesting triazo-compounds recently prepared and described by Forster and Fierz (this vol., 72, 669; also Proc., 1908, **24**, 102). Unlike the majority of the azoimides hitherto known, many of these triazo-compounds are liquids, and are therefore particularly suitable for a study of refractive and dispersive power.

Acknowledgment must here be made of the author's indebtedness to Dr. Forster and Dr. Fierz, who very kindly put at his disposal the materials required for this and the following investigation. Without their co-operation the work could not have been undertaken.

Two of the compounds examined, namely, phenylazoimide and benzylazoimide, were very kindly prepared by Dr. Fierz for the special purpose of this investigation. Two specimens of the former were made, one (*a*) by Emil Fischer's method, and the other (*b*) by Noelting and Michel's method. The specimen of benzylazoimide, prepared by heating benzyl chloride with sodium azide, boiled at 72° under a pressure of 8 mm.; on redistillation, the middle fraction, boiling at 64° under a pressure of 3 mm., was collected, but it was found that the molecular refraction was not altered by the redistillation. The description of the preparation and properties of triazoethyl alcohol, $N_3{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, another of the substances examined, will appear in a future communication by Dr. Forster and Dr. Fierz.

The refractive indices at 24·9° for the H_α, D, and H_γ lines were determined with a Pulfrich refractometer. A steady temperature was attained by circulating water from a thermostat by a small rotary pump in the way described by Lowry (*Trans. Faraday Soc.*, 1907, **3**, 119). This method of providing a current of water at constant temperature is very satisfactory, and may be highly recommended.

The densities of the various liquids were determined with a pyknometer, and the values recorded below are those obtained at 24·9°, the temperature at which the refractive indices were determined. The weighings were in all cases corrected for displaced air.

The observed values of density and refractive index are recorded in the following table:

TABLE I.

Substance.	d.	n_α.	n_D.	n_γ.
Ethyl triazoacetate	1·1191	1·43231	1·43487	1·44657
Ethyl α-triazopropionate	1·0583	1·42610	1·42857	1·43994
Ethyl β-triazopropionate	1·0798	1·43581	1·43833	1·45010
Ethyl bistriazoacetate	1·2204	1·46090	1·46400	1·47839
Triazoethyl alcohol	1·1435	1·45488	1·45778	1·47095
Bistriazoethane	1·1699	1·47629	1·47976	1·49583
Benzylazoimide	1·0655	1·52923	1·53414	1·55748
Ethyl triazoformate	1·1082	1·41353	1·41623	1·42861
Phenylazoimide (*a*)	1·0871	—	1·5588	—
,, (*b*)	1·0896	1·55227	1·55886	—
α-Naphthylazoimide	1·1713	1·64481	1·65501	—

The colour of phenylazoimide and α-naphthylazoimide prevented the determination of n_γ for these substances.

In the following table II are given in the second column the values of the molecular refraction $[\mathrm{M.R.}]_D = \frac{n_D^2 - 1}{n_D^2 + 2} \cdot \frac{M}{d}$; in the third column, the values of the molecular dispersion $[\mathrm{M.R.}]_\gamma - [\mathrm{M.R.}]_\alpha$; in the fourth column, the contribution to the molecular refraction which is to be assigned to the N_3-group, and in the fifth column the amount contributed to the dispersion by the N_3-group. Except where specially noted, the values in the fourth and fifth columns are obtained by subtracting from the experimental values of the molecular refraction or dispersion the total contributions of the other atoms in the molecule. For this purpose, the following values of the atomic refraction and dispersion have been employed: refraction, C, 2·501; H, 1·051; O (hydroxyl), 1·521; O (ether), 1·683; O (carbonyl), 2·287 (see Ostwald-Luther, *Physiko-chemische Messungen*, p. 234): dispersion, C, 0·039; H, 0·036; O (hydroxyl), 0·019; O (ether), 0·012; O (carbonyl), 0·086 (see Brühl, *Zeitsch. physikal. Chem.*, 1891, **7**, 191).

TABLE II.

			Contribution of N_3-group to	
Substance.	$[M.R.]_D$.	$[M.R.]_\gamma - [M.R.]_\alpha$.	Refraction.	Dispersion.
Ethyl triazoacetate	30·07	0·856	8·74	0·35
Ethyl α-triazopropionate......	34·80	0·977	8·87	0·36
Ethyl β-triazopropionate ...	34·79	0·984	8·86	0·37
Ethyl bistriazoacetate	38·42	1·242	9·07	0·38
Triazoethyl alcohol	20·75	0·626	8·97	0·35
Bistriazoethane..................	27·18	0·942	8·98	0·36
Benzylazoimide..................	38·82	1·701	8·85*	0·37*
Ethyl triazoformate	26·05	0·826	9·32	0·43
Phenylazoimide (*a*)	35·33	—	10·27*	—
,, (*b*)	35·25	—	10·19*	—
α-Naphthylazoimide	52·95	—	10·56†	—

* In these cases, the contributions of the phenyl and benzyl radicles have been obtained by subtracting the atomic refraction (or dispersion) of hydrogen from the molecular refraction (or dispersion) of benzene and toluene (for latter data, see Perkin, Trans., 1900, **77**, 273).

† The contribution of the α-naphthyl radicle was obtained by subtracting the atomic refraction of bromine from the molecular refraction of α-bromonaphthalene (see Brühl, *Zeitsch. physikal. Chem.*, 1897, **22**, 408).

The only one of these substances the refraction of which has already been determined is phenylazoimide. Brühl (*Zeitsch. physikal. Chem.*, 1894, **16**, 222) gives 35·93 as the value of $[M.R.]_D$ for this substance, whilst on the basis of Perkin's data (Trans., 1896, **69**, 1232) the value is 35·14. The values recorded in the foregoing table are in good agreement with Perkin's figure, and it is worthy of note that the specimen of phenylazoimide examined by him was prepared by a different method, namely, by the action of nitrosyl chloride on phenylhydrazine (Tilden and Millar, Trans., 1893, **63**, 256). Brühl's value is undoubtedly too high.

On reference to table II, it will be seen that, apart from ethyl triazoformate, phenylazoimide, and α-naphthylazoimide, the exceptional behaviour of which will be discussed later, the increment of the refraction or dispersion due to the N_3-group is remarkably uniform. Ethyl triazoacetate gives lower values than most of the substances, whilst ethyl bistriazoacetate, in which two N_3-groups are attached to the same carbon atom, gives figures which are rather above the average. The mean value of the increment in the refraction for the first seven compounds in the table is 8·91; the mean value of the increment in the dispersion is 0·36. From Brühl's researches, it appears that the atomic refraction of nitrogen in $\cdot NH_2$, as deduced from a study of the hydrazines, hydroxylamine, ammonia, and aliphatic amines, is 2·48, and the atomic dispersion 0·08. The optical effect therefore of the N_3-group, whether considered in reference to refraction or dispersion, is more than three times that of the single nitrogen atom in its simplest linkings. On the other hand, the value just deduced for the refraction of the N_3-group is not much greater than that found for the two nitrogen atoms in diazoacetic ester; according to Brühl, the value of $[M.R.]_D$ for this substance is 28·71, whence the increment due to the N_2-group is 8·43. The dispersion due to the two nitrogen atoms in diazoacetic ester is found by Brühl to be 0·90, or more than twice as great as the increment due to the three nitrogen atoms in the triazo-group.

Attention has frequently been directed (see, for example, Curtius, *Ber.*, 1896, **29**, 772) to the fact that a compound containing the N_3-group exhibits a marked similarity to the corresponding compound in which a halogen atom takes the place of this group. This parallelism is further emphasised by the values of the optical constants. The refraction increment due to the N_3-group is, as already stated, 8·91; the atomic refraction of bromine is 8·93. The dispersion increment due to the N_3-group is 0·36; the atomic dispersion of bromine is 0·35. This almost complete coincidence between the optical influence of the triazo-group and the bromine atom finds its first expression in the fact that the molecular refraction and dispersion of the triazo-compounds are practically the same as those of the corresponding bromine compounds. Thus, for example, the value of $[M.R.]_D$ for bistriazoethane is 27·18, and for ethylene dibromide, 26·99, whilst the molecular dispersions of the two substances are respectively 0·94 and 0·95. Again, the molecular refraction of ethyl α-triazopropionate is 34·80, whilst that of ethyl α-bromopropionate is 34·70.

In discussing the conclusions to be deduced from the data in table II, the abnormally high figures obtained for the refraction of ethyl triazoformate, phenylazoimide, and α-naphthylazoimide have not yet been considered. There appears to exist in these cases some special influence which raises the refraction increment for the N_3-group considerably above the normal value. This is best seen by comparing 8·85, the contribution due to the triazo-group in benzylazoimide, with 10·23, the mean value of the increment due to the same group in phenylazoimide. Such a different influence of the benzyl and phenyl groups on the refraction of an associated group has frequently been observed by earlier workers. Thus, for example, the refraction increment due to the $\cdot NH_2$-group is 4·41 in benzylamine, and 5·50 in aniline; the refraction increment due to the $\cdot CN$-group is 5·22 in phenylacetonitrile, and 6·53 in benzonitrile.

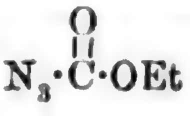
Not only is the refraction increment due to the N_3-group in ethyl triazoformate and phenyl- and α-naphthyl-azoimides abnormally high, but so also is the dispersion increment. So far as ethyl triazoformate is concerned, this will be obvious from table II, but, since n_γ could not be determined in the case of phenyl- and α-naphthyl-azoimides, it was not possible to test the dispersive power of these substances in the same way. The refractive indices, however, for the Hα and D lines were ascertained, and the values of $[\mathrm{M.R.}]_D$ and $[\mathrm{M.R.}]_D - [\mathrm{M.R.}]_\alpha$ have been worked out for these azoimides and the corresponding bromine compounds.

TABLE III.

Substance.	$[\mathrm{M.R.}]_D$.	$[\mathrm{M.R.}]_D - [\mathrm{M.R.}]_\alpha$.
Phenylazoimide	35·29	0·34
Bromobenzene	33·83	0·25
α-Naphthylazoimide	52·95	0·66
α-Bromonaphthalene	51·32	0·54

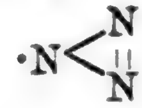
These figures show very clearly that the refractive and dispersive powers of the triazo-compound, instead of being, as one might expect, equal to those of the corresponding bromine compound, are very much higher.

The experimental data which have been submitted make it evident that the optical influence of the N_3-group is intensified in ethyl triazoformate, phenylazoimide, and α-naphthylazoimide, as compared with the other substances containing this group and enumerated in tables I and II. The question then arises whether any intelligible explanation can be given of such a difference in behaviour.

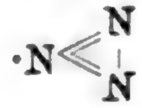
In this connexion, it is noteworthy that the phenomenon of a given group possessing an intensified optical influence in certain positions has been successfully referred to the contiguity of unsaturated groups. Brühl especially has shown (Trans., 1907, **91**, 115; *Ber.*, 1907, **40**, 878, 1153) that the presence in a molecule of the grouping C⁚C·C⁚C or C⁚C·C⁚O invariably produces a marked increase of both refractive and dispersive power (compare also Perkin and Kay, Trans., 1906, **89**, 839; Sir W. H. Perkin, Trans., 1907, **91**, 806; Smedley, this vol., 372). It is interesting therefore to find that in each of the triazo-compounds which exhibit exceptional optical behaviour, the N_3-group is adjacent to a doubly-linked carbon atom. In the case of ethyl triazoformate, this adjacent carbon atom is doubly linked to oxygen; in the cases of phenyl- and α-naphthyl-azoimides, the carbon atom which is linked to the N_3-group is also doubly linked to one of the adjacent carbon atoms in the ring. From this point of view, ethyl triazoformate,  $\mathrm{N_3{\cdot}\overset{\overset{O}{\|}}{C}{\cdot}OEt}$, may be compared with ethyl crotonate, $\mathrm{C_2H_4{⁚}CH{\cdot}\overset{\overset{O}{\|}}{C}{\cdot}OEt}$, the molecular refraction and dispersion of which are exceptionally high, whilst the effect of the contiguous ethylene linking on the optical influence of the N_3-group in phenyl- and α-naphthyl-azoimides is similar in kind to the effect of such a linking on the optical influence of the NH_2-group in *o*-toluidine.

Optically, therefore, the N_3-group behaves as an unsaturated complex. On analogy with the ethenoid group, one might be tempted to conclude that the particular nitrogen atom in the triazo-group which is linked to carbon must be doubly linked to one or both of the other nitrogen atoms. Such a conclusion, however, is hardly warranted, for Brühl has shown that the optical influence of the NH_2 and OH groups, in which there are no double linkings, is intensified in conjugation with the ethenoid group. The amino- and hydroxyl groups each contain an element the valencies of which are not all satisfied, and they may therefore be regarded as complexes with residual affinity. Since the N_3-group is built up out of one of these elements, it is not surprising that, so far as the optical evidence goes, it also should behave as a complex with residual affinity.

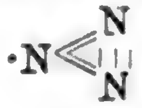
On the interesting question how the linkings of the three nitrogen atoms in the triazo-group should be represented, one fact at least brought out by this investigation throws some light. The complex N_3 may be represented in various ways, namely:


$\cdot\mathrm{N}{<}\begin{matrix}\mathrm{N}\\ \|\\ \mathrm{N}\end{matrix}$

I.


$\cdot\mathrm{N}{\ll}\begin{matrix}\mathrm{N}\\ |\\ \mathrm{N}\end{matrix}$

II.


$\cdot\mathrm{N}{\ll}\begin{matrix}\mathrm{N}\\ |||\\ \mathrm{N}\end{matrix}$

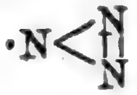
III.

$\cdot\mathrm{N}{:}\mathrm{N}{⋮}\mathrm{N}$

IV.

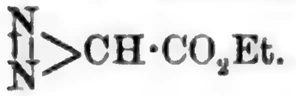
The first of these representations is the one which is generally employed by those who have occasion to deal with the N_3-complex, although it does not appear that there is any definite evidence in favour of formulation I as against the others. Some years ago (Proc., 1893, **9**, 57), Armstrong argued against the custom of representing phenylazoimide as $C_6H_5\cdot N{<}\begin{matrix}N\\ \|\\ N\end{matrix}$, suggesting that it might be regarded as a dinitrile, $\begin{matrix}{<}N-\underset{\displaystyle C_6H_5}{\overset{}{N}}-N{>}\end{matrix}$, on the assumption of the existence of latent affinities. The possibility of the formulation IV has recently been entertained by Forster and Fierz (this vol., 75), and compounds have been prepared by Dimroth (*Ber.*, 1907, **40**, 2376) which seem to show that the ring, if it exists, may be opened without difficulty. Thus the reduction of phenylazoimide leads readily to the formation of phenyltriazen, which, according to Dimroth's investigations, exists in two chemically isomeric forms; for these isomerides, the following formulæ are suggested: $C_6H_5\cdot N{:}N\cdot NH_2$ and $C_6H_5\cdot N{<}\begin{matrix}NH\\ |\\ NH\end{matrix}$.

The one fact brought out by this investigation which seems to have a bearing on the question is the relative optical influence of the diazo- and triazo-groups. It has already been pointed out that, whilst the refraction value for the N_3-group is normally 8·91, the refraction value of the N_2-group in ethyl diazoacetate is very little less, namely, 8·43, and, further, that the dispersion increment due to the *two* nitrogen atoms in ethyl diazoacetate is more than twice as great as the dispersion increment due to the *three* nitrogen atoms in ethyl triazoacetate and similar compounds. This is very striking, and lends support to the view that formulation I is to be preferred for the triazo-group, for it is the common experience of workers in this field that the accumulation of multiple linkings markedly raises the refraction and dispersion values, and the evidence just quoted shows that the optical influence of the triazo-group is relatively low. Consideration of the evidence, in fact, shows that formulations II, III, and IV for the triazo-group are unlikely, and that the arrangement

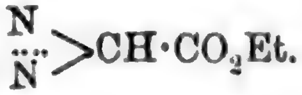


$\cdot N<\begin{matrix}N\\ \|\\ N\end{matrix}$ is the most probable.

If this view is adopted, it is difficult to account for the relatively much higher refractive and dispersive power of the diazo-group in ethyl diazoacetate on the basis of the ordinarily accepted formula:

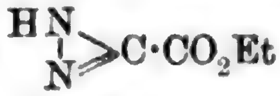


$\begin{matrix}N\\ \|\\ N\end{matrix}>CH\cdot CO_2Et$. The optical evidence taken alone would seem to suggest that one or both of the nitrogen atoms in ethyl diazoacetate are quinquevalent, as in the formula $N\vdots N\colon CH\cdot CO_2Et$ or



$$\begin{matrix}N\\ \vdots\\ N\end{matrix}>CH\cdot CO_2Et.$$

It is, indeed, customary to introduce quinquevalent nitrogen only in the formulation of compounds of the ammonium chloride type, but, in view of the optical evidence, the two foregoing formulæ cannot be ignored. The expression



$\begin{matrix}HN\\ |\\ N\end{matrix}\!\!>C\cdot CO_2Et$ for ethyl diazoacetate, although perhaps accounting for the optical exaltation by a Thiele conjugation, would involve a different type of structure for the higher members of the series, and, in absence of information relating to the optical properties of these, such an assumption would not be justified. Whatever be the explanation, the fact remains that the optical influence of the triazo-group is relatively lower than that of the diazo-group in similar compounds.

Brühl's discussion of the relative influence of the diazo- and triazo-groups (*Zeitsch. physikal. Chem.*, 1898, **25**, 597) is not convincing, since he compared the diazo-group in ethyl diazoacetate with the triazo-group in phenylazoimide; as has been shown in this paper, the latter compound exhibits an optical exaltation by reason of which such a comparison cannot be considered legitimate. In fact, Brühl himself admits that the optical constants of that nitrogen atom in phenylazoimide which is next the benzene ring are possibly higher than the normal values.

It has not yet been possible to examine triazen derivatives in which the nitrogen atoms are undoubtedly arranged in an open chain. When this can be done, further interesting information as to the spectrochemistry of nitrogen, and possibly as to the relation of the nitrogen atoms in the triazo-group, will be available.

ROYAL COLLEGE OF SCIENCE,
LONDON, S.W.

LXXXVI.—*The Dissociation Constants of Triazoacetic and α-Triazopropionic Acids.*

By JAMES CHARLES PHILIP.

IT has been generally recognised that the behaviour of azoimide is in many respects similar to that of the hydrogen halides. The similarity, however, does not extend to all their properties, for, whilst hydrogen chloride, hydrogen bromide, and hydrogen iodide in aqueous solution are among the strongest acids known, azoimide is only feebly acidic, approximately equal in strength to acetic acid (Curtius and Radenhausen, *J. pr. Chem.*, 1891, [ii], **43**, 207; West, Trans., 1900, **77**, 705). Since the preparation of triazoacetic and α-triazopropionic acids by Forster and Fierz (this vol., pp. 72 and 669), a little more material is available for the study of the way in which the strength of an acid is affected by the substitution of the triazo-group for a halogen atom. The dissociation constants of triazoacetic and α-triazopropionic acids have therefore been determined, specimens of the two compounds being very kindly supplied by Dr. Forster.

The conductivity of various solutions of the acids and of their sodium salts was determined at 25° by the usual Kohlrausch method. The pure redistilled water employed in making up and diluting the solutions had a specific conductivity of 2×10^{-6} at 25°. A correction was made for this in the case of the sodium salt solutions only. These last were prepared by exactly neutralising a known quantity of standard sodium hydroxide with the acid under examination.

The equivalent conductivities of the sodium salts at infinite dilution were found by extrapolation from the observed values in the way suggested by Bredig (*Zeitsch. physikal. Chem.*, 1894, **13**, 191). For sodium triazoacetate, $\lambda_\infty = 91$, the same as the corresponding figure for sodium monobromoacetate; for sodium α-triazopropionate, $\lambda_\infty = 87$, which is also the value for sodium α-bromopropionate. If the ionic conductivity of hydrogen at 25° is taken as 350, and that of sodium as 51, the values of λ_∞ at this temperature for triazoacetic and α-triazopropionic acids are respectively 390 and 386.

The results obtained for the conductivity of the acids are recorded in the following tables.

Triazoacetic Acid.

Mols. per litre.	λ.	$\alpha = \frac{\lambda}{\lambda_\infty}$.	$K = \frac{\alpha^2}{(1-\alpha)V}$.
0·0698	43·7	0·112	0·00099
0 0349	59·5	0·153	0·00096
0·01745	80·1	0·205	0·00093
0·00698	117·1	0·300	0·00090
0·00349	151·6	0·389	0·00086

α-Triazopropionic Acid.

Mols. per litre.	λ.	$\alpha = \frac{\lambda}{\lambda_\infty}$.	$K = \frac{\alpha^2}{(1-\alpha)V}$.
0·0614	43·4	0·112	0·00088
0·0307	59·9	0·155	0·00088
0·01535	81·2	0·210	0·00086
0·00614	119·6	0·310	0·00086
0 00307	155·5	0·403	0 00084

The values of the expression $\frac{\alpha^2}{(1-\alpha)V}$, instead of being independent of the dilution as might be expected, show a distinct decrease in the case of triazoacetic acid and a slight decrease in the case of α-triazopropionic acid. The cause of this is probably a slight trace of sulphuric acid in the specimens of the acids. The apparatus and method of work were tested by determining the conductivity of potassium chloride solutions; values were obtained in close agreement at all dilutions with the figures recorded by Ostwald, Bredig, and Walden, so that the diminution in the value of K for triazoacetic and α-triazopropionic acids cannot be attributed to errors in the determination of the conductivity. It was thought that it might be due to some slight decomposition promoted by the finely-divided platinum on the electrodes, but this explanation was discounted by the observation that the resistance of a solution of triazoacetic acid did not change during several hours' contact with the platinised platinum electrodes of the conductivity cell. It appears therefore most probable that the specimens of the acids which were used contained a slight trace of sulphuric acid, which would be sufficient to account for the diminution in the value of K with dilution. Sulphuric acid was used in the preparation of the specimens, and, as it was not possible to purify the acids by distillation or crystallisation (see Forster and Fierz, *loc. cit.*), the presence of such an impurity is not improbable.

In spite of the fact that the value of K decreases on dilution, it will be sufficient for the purpose of this investigation to take for the dissociation constant the mean of the figures given in the foregoing tables. Hence, for triazoacetic acid, $100K = 0{\cdot}093$; for α-triazopropionic acid, $100K = 0{\cdot}086$. It is instructive to compare with these the values of $100K$ for the corresponding halogen derivatives of acetic and propionic acids:

	$100\,K$.
Monochloroacetic acid..................	0·155
Monobromoacetic acid	0·138
Monoiodoacetic acid	0·075
α-Bromopropionic acid	0·108

From these figures, it will be seen that the introduction of a triazo-group into the molecule of acetic acid has an effect on the strength of the acid which is rather less than that due to a bromine atom and rather greater than that due to an iodine atom. This result is further evidence of similarity in the functions of the triazo-group and a halogen atom.

Royal College of Science,
London, S.W.

LXXXVII.—*The Spontaneous Crystallisation of Substances which form a Continuous Series of Mixed Crystals. Mixtures of Naphthalene and β-Naphthol.*

By Henry A. Miers, F.R.S., and Florence Isaac.

Our study of spontaneous crystallisation has, up to the present, been confined to mixtures in which the components crystallise out in the pure state alone, such as mixtures of salol and betol, aqueous solutions of sodium nitrate, sodium chlorate, etc., and mixtures of sodium nitrate and lead nitrate in water.

The present investigation deals with the spontaneous crystallisation of mixtures of naphthalene and β-naphthol, which are said to form a continuous series of mixed crystals, and also with the freezing- and melting-point curves for these mixtures.

Mixed crystals of naphthalene and β-naphthol have been investigated by van Bijlert (*Zeitsch. physikal. Chem.*, 1891, **8**, 362), Crompton and Whiteley (Trans., 1895, **67**, 333), Küster (*Zeitsch. physikal. Chem.*, 1895, **17**, 360), and Bruni (*Rend. Accad. Lincei*, 1898, **2**, 138). The addition of naphthalene to β-naphthol depresses the freezing point, and it was found by Küster that the depression is proportional to the amount of naphthalene added, so that the freezing-point curve was stated by him to be a straight line joining the melting points of the two components. He admitted that this was directly opposed to the experimental result of van Bijlert, who came to the conclusion that "in a solution of β-naphthol in molten naphthalene, a solid solution separates which is considerably richer in β-naphthol than is the remaining mother liquor."

Since Küster's conclusions are directly opposed to the generally accepted theoretical considerations, experiments were made by Bruni in which the freezing points of the crystals and of the liquid from which they have separated were determined independently; he concluded that the crystals always possessed a freezing point somewhat above that of the original solution and were richer in β-naphthol, whilst the remaining liquid possessed a lower freezing point and was poorer in β-naphthol.

The Crystals of Naphthalene, β-Naphthol, and their Mixtures.

The crystalline form of naphthalene has been described by Groth (*Physikalische Krystallographie*, 1905, p. 380) and by Negri (*Gazzetta*, 1893, **23**, ii, 375).

The crystalline form of β-naphthol has also been described by Groth (*Annalen*, 1865, **152**, 285) and by Liweh (*Zeitsch. Kryst. Min.*, 1886, **11**, 249).

No further goniometric measurements were therefore made by us, but naphthalene, β-naphthol, and their mixtures were examined under the microscope with a view to their identification in minute crystals. The microscope was fitted with a heating stage by means of which the crystals could be melted by a small gas flame placed under the stage or could be allowed to grow by sudden cooling. The cooling was effected by means of an arrangement of two tubes through which a current of cool air could be forced on to the surface of the microscope slide or cover glass.

Naphthalene.—A drop of a solution of naphthalene in alcohol, placed on a microscope slide under a cover glass and allowed to evaporate slowly, gives plates of naphthalene of rhombic outline, having an approximate angle of 71°20′ and diagonal extinction. The angle of the rhomb calculated from the measurements of Groth and Negri is 71°16′. The interference figure shows one optic axis lying in the plane of the longer diagonal of the rhomb and visible on the edge of the field, and the birefringence about the normal to the plate is positive. The angle between the direction of emergence of the optic axis and the normal to the crystal plate is 42°30′ approximately, as measured by means of a micrometer eyepiece. All the rhombs which appear correspond precisely with the above description, except that in a few cases the acute angle of the rhomb is truncated by a small face equally inclined to the two edges, thus giving it a hexagonal appearance.

Naphthalene allowed to crystallise from other solvents in the same manner under a cover glass on a microscope slide, or from the pure fused substance, yields crystals identical in all respects with the above.

β-Naphthol.—Examined under the microscope on the heating stage described above, β-naphthol crystallised from a solution in water in rhombs having an approximate angle of 71° and diagonal extinction. The angle of the rhomb calculated from previous measurements is 72°2′. The interference figure showed one optic axis on the edge of the field, and the birefringence about the normal is positive. The angle between the direction of emergence of the optic axis and the normal to the crystal plate is again approximately 42°30′. Therefore by mere examination under the microscope, it is impossible to distinguish a rhomb of naphthalene from one of β-naphthol.

β-Naphthol was also examined while crystallising from fusion under a cover glass. The interference figure was always the same as that described above, but the crystals spread out so rapidly in a thin sheet, in spite of the gas flame under the stage, that it was impossible to measure any angles of the rhombs, their outline being quite indistinguishable.

Mixtures of Naphthalene and β-Naphthol.—Owing to the high temperature at which the mixed crystals of naphthalene and β-naphthol form, namely, between 79·5° and 121° for the various mixtures, it has not been found possible to isolate them for the measurement of their angles on the goniometer. The mixed crystals from the fused mixtures are always very thin plates or needles, which break up and become opaque as soon as they are touched.

The fused mixtures have, however, been examined by the microscope as they solidified under a cover glass. Like the crystals of β-naphthol, the mixed crystals always spread out so rapidly under the cover glass that they showed no distinguishable outline. Their interference figures, however, could be determined. Three mixtures were examined, namely, naphthalene 80 per cent., and β-naphthol 20 per cent.; naphthalene 50 per cent., and β-naphthol 50 per cent., and naphthalene 30 per cent., and β-naphthol 70 per cent. These all gave precisely the same interference figure, having one optic axis visible on the edge of the field and positive birefringence; thus completely resembling the pure constituents. Further, the angle between the direction of emergence of the optic axis and the normal to the plate is always approximately 42°30′.

Thus, under the microscope, it is impossible to distinguish between naphthalene, β-naphthol, and the various mixed crystals.

This is unfortunate, because one of the chief objects of the present investigation was to ascertain the composition of the mixed crystals which separate spontaneously from a given solution, and it was hoped that this might be done by the exact determination of their optical characters.

The Curve of Spontaneous Crystallisation.—In the experiments on the temperature of spontaneous crystallisation of naphthalene, β-naphthol, and their mixtures, the method adopted was one that had been used in the previous experiments on spontaneous crystallisation.

The mixture was placed in a tube of Jena glass, which also contained some angular fragments of glass, and the tube was sealed. It was then heated in boiling water, hot brine, or olive oil, and the tube shaken thoroughly until all the crystals had completely melted. The tube was then allowed to cool gradually in a large beaker containing either water, brine, or olive oil, and was shaken continually by hand. The liquid in the beaker was kept continually stirred by a small revolving platinum vane driven by an electric motor, and two thermometers, one at the top and the other at the bottom of the beaker, showed the temperature of the liquid to be uniform throughout. When the temperature had fallen to a certain point, crystals made their appearance suddenly in the sealed glass tube, this temperature depending on the constitution of the mixture in the tube. The crystals which first appear in the tubes are thin, rhombic plates, which reflect light in bright colours, long crystal needles next appear and grow rapidly through the tube, and finally the whole mass solidifies and becomes opaque.

On page 931 are given the results of these experiments, each of which was repeated several times.

These results plotted on a concentration-temperature diagram give the supersolubility curve or curve of spontaneous crystallisation for all possible mixtures of naphthalene and β-naphthol. It will be seen from the diagram that this curve is very nearly a straight line joining the temperatures of spontaneous crystallisation of the pure components, namely, 77° for pure naphthalene and 117·5° for pure β-naphthol.

The method of tracing the supersolubility curve or curve of spontaneous crystallisation by means of the change in the index of refraction, which has been used in all our previous work on spontaneous crystallisation, was not applied in these experiments, for the high temperatures involved render the method inconvenient; further difficulties are introduced by the fact that both naphthalene and β-naphthol sublime very readily, and it is therefore almost impossible to prevent inoculation in an open vessel, such as the trough of the goniometer.

Percentage constitution of mixture in tube.		Method of heating to dissolve crystals.	Temperature of spontaneous crystallisation.
Naphthalene.	β-Naphthol.		
100	0	In boiling water for 10 mins., 15 mins., and for 2 hours	77°
90·065	9·935	In boiling water for various lengths of time	80·5
80·08	19·92	In boiling water for half an hour several times	84
70·066	29·934	Heated to 101° in brine for various lengths of time	89·1
60·38	39·62	Heated in brine to 101° for various lengths of time	92·75
49·663	50·337	Heated for 15 mins. in olive oil to 110—115°	96·5
40·615	59·385	Heated for 15 mins. in olive oil to 120°	101
31·877	68·123	Heated for 15 mins. in olive oil to 120°	104·2
20·03	79·97	Heated in olive oil for 15 mins. to 120°	108·8
9·227	90·773	Heated in olive oil	113
0	100	Heated in olive oil	117·5

The Freezing- and Melting-Point Curves for Mixtures of Naphthalene and β-Naphthol.

Since naphthalene and β-naphthol are miscible with one another in all proportions, the solid solution and the liquid solution, which are in equilibrium with each other, have to be distinguished; the concentration of the components in the two being in general different. It should therefore be possible to determine for mixtures of naphthalene and β-naphthol (1) the freezing-point curve, giving the temperatures at which solid begins to be deposited from the liquid solution; and (2) the melting-point curve, giving the temperatures at which solid solutions just begin to liquefy.

Since naphthalene and β-naphthol form a continuous series of mixed crystals, these curves will also be continuous, and both the freezing points of different liquid solutions and the melting points of different solid solutions will lie between the melting points of the pure components.

(1) *The Freezing-Point Curve.*—In the experiments on the freezing-point curve for these mixtures, the same sealed tubes containing mixtures of various constitutions were used as in the preceding experiments on spontaneous crystallisation.

Each tube was heated in an oil-bath until all the crystals had completely melted. It was then held outside the bath for a few seconds until a few crystal needles just began to grow at the bottom or top of the tube. The tube was then immediately re-immersed and shaken by hand in the oil-bath, the temperature of which was then allowed to fall very slowly, and the few small crystal needles were watched carefully. Above a certain temperature, the crystals always dissolved completely, and the entire experiment was repeated several times, the temperature of the oil-bath being lowered one or two degrees between each experiment. When, however, the oil-bath had reached a certain temperature, on re-immersing the tube containing a few crystal needles, and allowing the temperature to continue to fall very slowly, at a certain temperature the crystal needles were at last seen to grow slowly, or some of them at first dissolved and then new crystals formed and grew gradually in the liquid mixture.

This temperature is taken to be very approximately the freezing point of the liquid mixture, since at this point solid first begins to separate from the inoculated liquid.

The experiment was repeated five or six times for each mixture used, and the mean of the results obtained in each case was taken as the true freezing point of the mixture. All the freezing points are thus determined with a falling temperature. The results appear tabulated on pp. 933 and 934 and also in the diagram, which gives the freezing-point curve for all mixtures of naphthalene and β-naphthol.

(2) *The Melting-Point Curve.*—An approximation to the melting-point curve for mixtures of naphthalene and β-naphthol was obtained in a somewhat similar manner. The same tubes were used as in the above experiments, and they were again immersed in a hot oil-bath. A few crystal needles were allowed to form in each tube in the manner described above, the temperature of the oil-bath was lowered, and the crystals allowed to grow slowly until the temperature had fallen to within one degree of the temperature of spontaneous crystallisation of the mixture as given by the previous experiments.

The oil-bath was then heated again, and the crystals in the tube were watched as the temperature rose, the tube being shaken continuously as before. At first they continue to grow or appear to remain stationary; when, however, a certain temperature is reached, the crystal needles, which have now grown so as to constitute a large part of the mixture, begin to melt, and their sharp edges become quite rounded. This temperature is taken to be approximately the melting point of the solid having the constitution of the original mixture. The experiment was repeated several times for each mixture, and the mean temperature obtained in each case was taken as the melting point of that mixture. The temperature thus obtained must in reality be a little too high, so that the true melting-point curve should doubtless be separated rather more widely from the freezing-point curve than it is in the diagram.

All the melting points are thus determined with a rising temperature. These results also appear tabulated below and in the diagram, and together they give the melting-point curve for all mixtures of naphthalene and β-naphthol.

Description of Oil-bath.—The oil-bath used was a large, wide glass beaker. Its sides were covered with a velvet case, in which were cut two small windows opposite each other half-way down the beaker, so that light may be passed through the beaker. An electric light with a ground glass bulb was placed behind one of these windows, and a lens was placed between the light and the window so as to throw a beam of light on the tube immersed in the oil. The tube was observed with a lens through the other small window in the front of the beaker in a darkened room.

The oil-bath was heated in the first place by means of a Bunsen burner, but during the actual experiments a small Argand burner was placed immediately beneath it. This small flame could easily be regulated so as to keep the bath at a constant temperature if desired, or to allow the temperature to rise or fall very slowly, for example, by one degree in a quarter of an hour. The oil was stirred throughout the experiments with a revolving platinum vane driven by an electric motor, and also by hand by agitating the immersed tube. Thermometers showed that the temperature of the bath was always uniform throughout.

The readings for the temperatures of the melting and freezing points were taken on a thermometer reading to a tenth of a degree.

Tabulated Results of Above Experiments.

Percentage concentration.			
Naphthalene.	β-Naphthol.	Freezing point.	Melting point.
100	0	79·5°	79·5°
90·065	9·935	84·5°, 84·9°, 84·2°, 84·5°, 84·9°. Mean, 84·6°.	83·4°, 82·7°, 83·5°, 82·9°, 82·7°. Mean, 83·04°.
80·08	19·92	88·1°, 88·9°, 88·7°, 88·5°. Mean, 88·55°.	87·5°, 87·2°, 87·3°. Mean, 87·33°.
70·066	29·934	92·5°, 92·5°, 92·5°. Mean, 92·5°.	91·5°, 91·5°, 91·5°. Mean, 91·5°.
60·38	39·62	98°, 97·7°, 97·7°, 97°, 97°, 97·5°. Mean, 97·5°.	95·7°, 95·5°, 95·5°, 94·8°, 95·5°. Mean, 95·4°.

Tabulated Results of Above Experiments (continued).

Percentage concentration.			
Naphthalene.	β-Naphthol.	Freezing point.	Melting point.
49·663	50·337	102°, 102·2°, 101·5°, 101·8°, 102°, 101·4°. Mean, 101·8°.	100°, 99·3°, 99·5°, 99·7°, 99·5°, 99·5°. Mean, 99·6°.
40·615	59·385	106°, 105·5°, 105·5°, 105°, 105°. Mean, 105·4°.	103·1°, 103·5°, 103·3°, 103°, 103·4°, 103·1°. Mean, 103·23°.
31·877	68·123	109°, 108·5°, 109°, 108·8°, 109°, 109·1°. Mean, 108·9°.	107·3°, 106·8°, 107·2°, 107·4°, 107·2°. Mean, 107·2°.
20·03	79·97	113°, 113·3°, 113°, 113·1°, 113·3°, 113·4°, Mean, 113·2°.	112·4°, 112·5°, 112·3°, 112·5°, 112·5°, 112·5°. Mean, 112·45°.
9·227	90·773	118°, 117·8°, 117·9°. Mean, 117·9°.	117·2°, 117·3°. Mean, 117·25°.
0	100	121°.	121°.

The freezing- and melting-point curves are shown on the diagram, and also the supersolubility curve, or curve of spontaneous crystallisation. The freezing-point curve is slightly above, and the melting-point curve slightly below, the straight line which joins the melting points of the pure components.

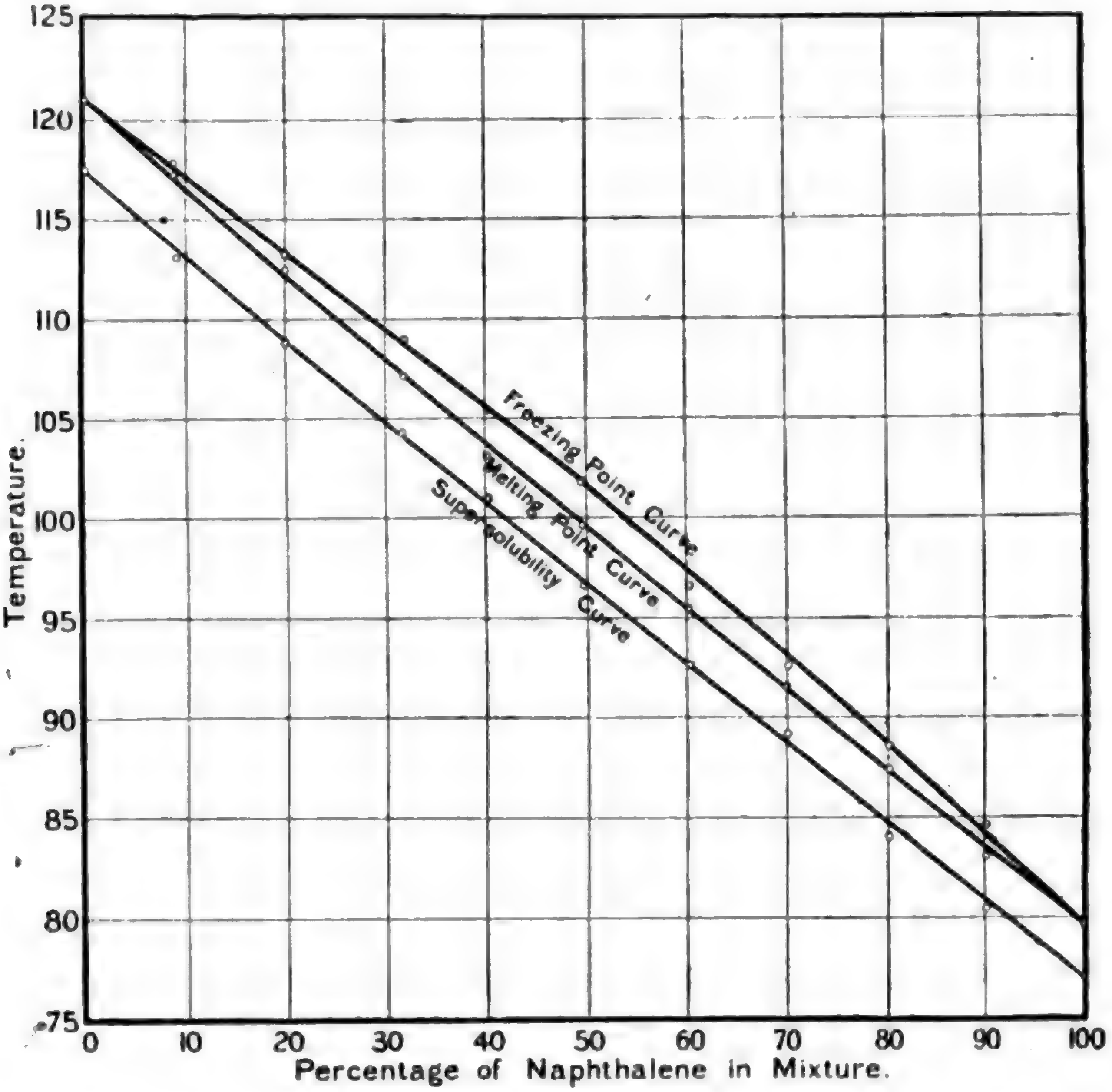
These experiments completely confirm and extend these observations of van Bijlert and Bruni, but do not support the assertion of Küster that the freezing-point curve for mixtures of naphthalene and β-naphthol is the straight line which joins the melting points of the two components.

The diagram shows the supersolubility curve to be separated from the melting-point curve by an interval of about 3° of temperature The metastable area (that is, the area in which crystals will not fo spontaneously in a supersaturated solution, but will only grow inoculation) for these mixtures is therefore very much narrower it has been found to be for any of the aqueous solutions or mixtures hitherto examined, in which the melting-point curve and supersolubility curve are generally separated by an interval of at least 10° of temperature.

It is interesting to compare the numbers obtained from the curves which we have established with an observation quoted by Küster from van Bijlert's paper, that a fusion containing 9·08 per cent. of β-naphthol yields crystals containing 11·5 per cent. of β-naphthol, the remaining mother liquor containing 8·5 per cent.

Comparison with the freezing- and melting-point curves given above shows that, according to our experiments, an inoculated fusion containing 9 per cent of β-naphthol would at first yield crystals containing 10·75 per cent. of β-naphthol, whilst the final composition of the mother liquor would be β-naphthol 8·3 per cent., and naphthalene 91·7 per cent.

We may also compare with our curves the observation of Bruni that during solidification a fusion containing approximately 50 per cent. of β-naphthol fell more than 2° in temperature. The figure shows that an inoculated fusion of 50 per cent. of naphthalene and 50 per cent. of β-naphthol should begin to freeze at 102·6°, and under suitable conditions complete solidification would occur at 99·3°, so that the fall of temperature during solidification should be about 3·3°.



Finally, it may be remarked that, although our experiments have failed to determine for these mixtures the exact composition of the crystals which separate from a given solution, they do suggest that this is quite definite, for each solution crystallises spontanoously at a definite temperature. If the composition of the crystals could vary in different experiments upon the same solution, it is probable that the temperature of spontaneous crystallisation would vary also, and it might have been expected that this would happen.

MINERAL DEPARTMENT,
UNIVERSITY MUSEUM, OXFORD.

LXXXVIII.—*The Influence of Solvents on the Rotation of Optically Active Compounds. Part XII. Ethyl Tartrate in Aromatic Halogen Derivatives.*

By THOMAS STEWART PATTERSON and DAVID PATERSON McDONALD, M.A., B.Sc.

IN continuation of this investigation, the last part of which (Trans., 1908, **93**, 355) dealt with the behaviour of certain aliphatic halogen derivatives, we have examined the solvent influence of a number of aromatic halogen substitution products on the rotation of ethyl tartrate, the procedure being exactly the same as formerly described.

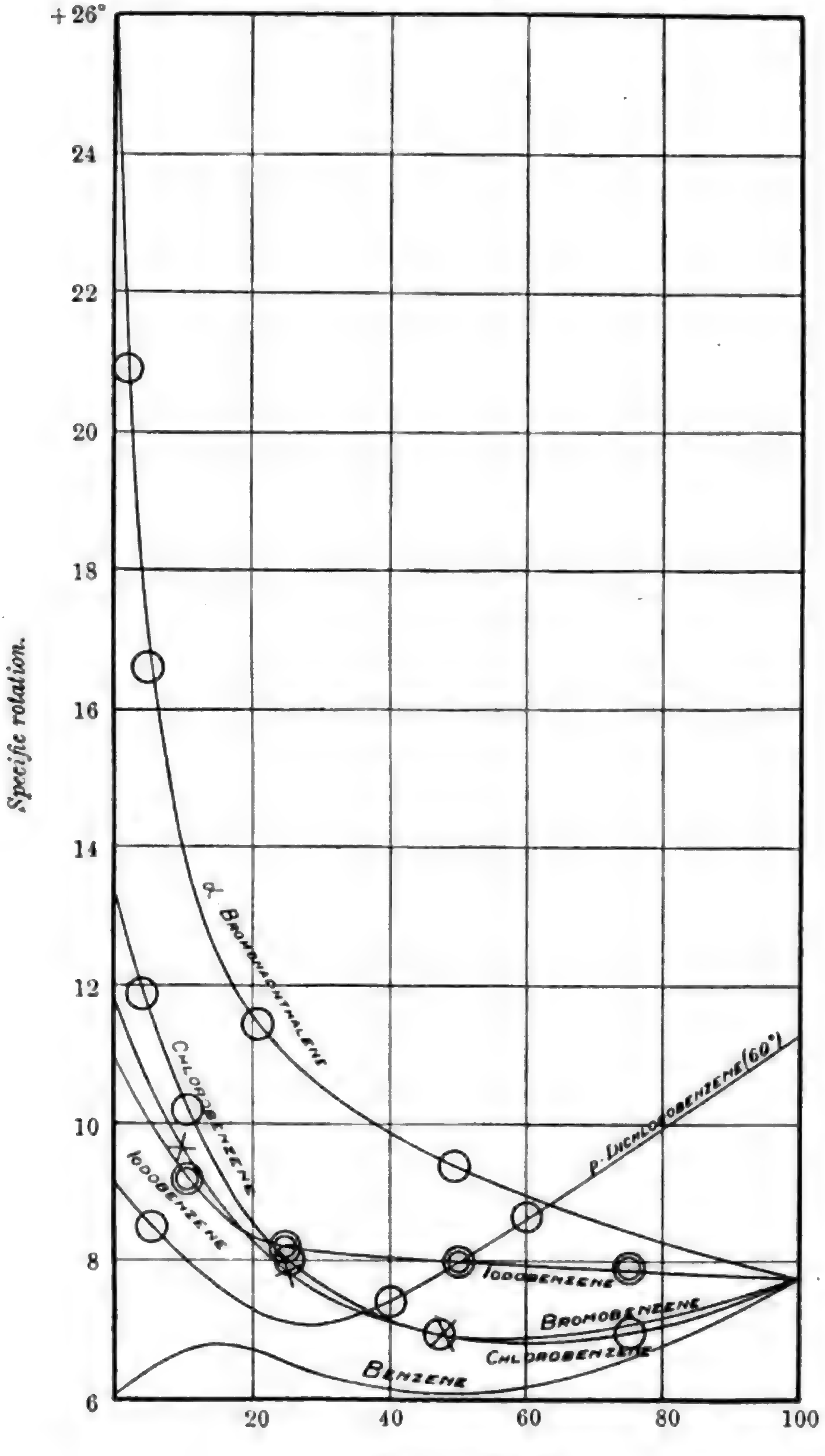
The numerical data are collected together at the end of the paper, but the main points of interest are brought out by the diagram, in which are shown curves representing the variation of the specific rotation of ethyl tartrate with change of concentration in the various solvents used.

We may consider first the curves of chloro-, bromo-, and iodo-benzene. It will be observed that they are of a similar character and that, as might have been expected, they show a progressive variation.

Addition of chlorobenzene at 20° to ethyl tartrate gradually lowers the specific rotation of the ester from $+7{\cdot}76°$ until a distinct minimum of $+6{\cdot}8°$ is reached at, or near, $p=58$. With further dilution, the specific rotation rises again, reaching the original value at about $p=27$, and continuing to rise at an increasing rate as the solution becomes more dilute, attaining, finally, to a value of $+13{\cdot}3°$ at infinite dilution.

The solvent effect of bromobenzene is of a very similar character, but the initial lowering of the rotation is not so great. A minimum rotation of about $+6{\cdot}93°$ occurs at practically the same concentration as in chlorobenzene, but the subsequent rise in rotation is not so rapid, so that the two curves intersect at about $p=30$. The rotation in bromobenzene at infinite dilution would be $+11{\cdot}8°$.

Ethyl tartrate in benzene, chlorobenzene, bromobenzene, iodobenzene, and α-bromonaphthalene at 20° and in p*-dichlorobenzene at 60°.*



The chlorobenzene curve is marked by circles, that for bromobenzene by crosses, and that for iodobenzene by concentric circles.

With the substitution of an iodine atom in the molecule, the rotation of the dissolved ester constantly rises, slowly at first, and much more rapidly in dilute solution, reaching a final value at infinite dilution of +11°. There is in this solvent at 20° no concentration of minimum rotation.*

A number of interesting comparisons can be instituted between these solvents and others previously examined. For this purpose, the curve for benzene (Trans., 1902, **81**, 1098) is shown in the diagram, and it will be observed that in fairly concentrated solutions, down to about $p = 30$, the behaviour of benzene is similar to that of its monochloro- and monobromo-derivative. Dilution of ethyl tartrate with any of these three substances causes initial diminution of the rotation of the ester. A minimum rotation occurs at practically the same concentration in each case. This resemblance in behaviour ceases, however, in more dilute solutions, since in benzene a maximum rotation is reached at $p = 12$, and in solutions less concentrated than this the rotation diminishes instead of increasing with further dilution.

Between the curves for chloro-, bromo-, and iodo-benzene and those for the aliphatic halogen derivatives there is, on the whole, a striking contrast. The latter solvents in all cases examined and at all concentrations depressed the rotation of ethyl tartrate considerably below that of the homogeneous ester, and, at least in a number of important instances, this diminution becomes more rapid with increasing dilution, so that in such cases the action of the two classes of solvents is exactly of an opposite character. Concentrations of minimum rotation occur in the aliphatic halides, but these are by no means so pronounced as in chlorobenzene and bromobenzene. In any case, concentrations of minimum rotation cannot be regarded as characteristic of any one series of solvents, as they appear to occur in all classes, particularly at low temperatures.

In the figure is also shown a curve for *p*-dichlorobenzene, but in this case, since the solvent easily crystallises out even from solutions containing a considerable proportion of tartrate, the polarimetric observations could only be extended down to a temperature of about 50°. The concentration curve shown is for 60°. It is obvious, of course, that the concentration-rotation curve for *p*-dichlorobenzene at 20° would lie much below that for benzene. A rough idea of what its appearance would be may be obtained by imagining the curve for 60° lowered on the diagram so that the point on it for $p = 100$ coincides with the point common to all the other curves. It will be observed that dilution of ethyl tartrate with *p*-dichlorobenzene also diminishes the rotation of the ester from 11·3° ($p=100$) until a concentration of about $p=25$ is reached, at which a minimum rotation (+7·1°) occurs. Further dilution brings about a slight rise in rotation. Thus, comparing benzene, chlorobenzene, and *p*-dichlorobenzene, it appears that, whereas the introduction of one chlorine atom in the molecule of the solvent causes increase in the rotation of the dissolved ester, a second chlorine atom in the para-position produces a solvent having a greater depressing effect than the mother substance.

---

* Separation of iodine seemed to take place somewhat more rapidly from the solutions than from the pure solvent. After the solutions had stood overnight, their rotation had always diminished slightly.

In all three cases, a concentration of minimum rotation is distinctly marked.

We have also determined the molecular solution-volume of ethyl tartrate in the monohalogen substitution derivatives * for comparison with the corresponding rotations, since, from previous work, it might be expected that these variables should show an inverse relationship. In the solvents mentioned, for concentrations below about $p=20$, both rotation and molecular solution-volume increase rapidly, which is apparently in opposition to the regularity referred to. It is, however, only on the limiting value of the solution-volume that any valid arguments can be based (Trans., 1901, **79**, 192), but, unfortunately, in the instances under consideration the increase of molecular solution-volume is so rapid in dilute solution that it is very difficult by extrapolation to arrive at any satisfactory estimate for the value at infinite dilution. Therefore, in the table below, the figures for solution-volume are given for $p=5$, whilst those for rotation are for $p=0$:

Ethyl tartrate in	M.S.V.$^{20°}$. $p=5$.	$[\alpha]_D^{20°}$ infinite dilution.
Chlorobenzene	173·71 c.c.	+13·3°
Bromobenzene...............	174·91 ,,	11·7
Iodobenzene	175·38 ,,	11·0

It will be seen that the inverse relationship does appear to hold for the solvents in question, but it must be admitted that the data for molecular solution-volume are somewhat unsatisfactory, since, on account of the rapid increase of volume in dilute solution and on account of the fact that any small error in the density determination of dilute solutions is greatly magnified in the process of calculation, it is difficult definitely to decide whether or no at low concentrations the solution-volume curves intersect like those for rotation.

It may further be noticed that in these solvents, as in the aliphatic halogen derivatives (Trans., 1908, **93**, 355), ethyl tartrate has in general the greatest volume in iodides and the least in chlorides. This is shown by the preceding table and by the one on p. 940.

---

* In a solvent like *p*-dichlorobenzene, trustworthy values for molecular solution-volume could hardly be obtained.

Ethyl tartrate in	Infinite dilution.	
	M.S.V.$^{20°}$ in c.c.	$[\alpha]_D^{20°}$.
Ethyl iodide	178·3	−2·2°
Ethyl bromide	172·6	−0·95
Ethylene bromide	176·8	−20·0
Ethylene chloride	176·0	−4·1
Acetylene tetrabromide	176·6	−18·8
Acetylene tetrachloride	173·6	−16·6

Ethyl tartrate in	Infinite dilution.	
	M.S.V.$^{20°}$ in c.c.	$[\alpha]_D^{20°}$.
Methylene iodide	177·7	−0·8°
($p=1·4$).		
Methylene chloride	174·1	−1·6
Bromoform	177·1	+0·2
Chloroform	175·0*	−3·0

In all these cases, the volume of the ethyl tartrate is greater in iodides than in bromides, and greater in bromides than in chlorides. In the three instances on the left of the table, the greater volume is associated with the lower rotation, whilst in the other two cases the opposite obtains.

In an earlier paper (Trans., 1902, **81**, 1134), it was shown by one of us that naphthalene as a solvent has a very marked influence on the rotation of ethyl tartrate, an influence distinctly different from that of benzene. It was of interest to ascertain whether a similar difference exists between the monohalogen derivatives of benzene and naphthalene respectively, and therefore we have investigated the solvent effect on ethyl tartrate of α-bromonaphthalene, the concentration-rotation curve being reproduced in the diagram. It will be noticed that the curve for α-bromonaphthalene is similar both to those for bromobenzene (although there is no concentration of minimum rotation at 20°) and for naphthalene in what is, perhaps, the most important particular, namely, rapid increase of specific rotation with diminishing concentration, especially in dilute solution. In α-bromonaphthalene this is very striking indeed, the rotation increasing from 16·5° for $p=5$ to 20·9° for $p=2$. It is not possible to give an accurate estimate for the value of the specific rotation at infinite dilution, but it probably is nearly +26°. It is difficult to say whether the value for the solution-volume of ethyl tartrate is in agreement with that for the rotation or not. For $p=5$ the molecular solution-volume is 174·2 c.c., which is a little greater than in a chlorobenzene solution of the same strength, but is less than in bromo- and

---

* In the last part of this research (Trans., 1908, **93**, 357, note), the opinion was expressed that the value formerly estimated (Trans., 1905, **87**, 320) for the M.S.V. of ethyl tartrate in chloroform might be too high, this idea being formed from a comparison of the M.S.V. curve for chloroform with the curves for other solvents. We have, therefore, re-examined the matter and have obtained the following data:

p.	d.	δ.	M.S.V.$^{20°}$.
3·00068	1·47773	1·48864	172·43 c.c.
4·00196	1·47425	1·48864	172·13 ,,
5·92138	1·46783	1·48881	171·90 ,,

Taking the new data along with those formerly found, a mean value of about 175 c.c. is obtained for M.S.V.$^{20°}$ at infinite dilution.

iodo-benzene. The form of the solution-volume curve is such, however, as makes it highly probable that at infinite dilution the volume of the ester in α-bromonaphthalene is distinctly less than in the other three solvents, which is, so far, in agreement with the suggested inverse relationship of rotation and volume.

In regard to the effect of temperature change, the rotation of solutions of ethyl tartrate in α-bromonaphthalene are of some special interest. It has been noticed already in the course of this investigation that when the effect of a large excess of a given solvent is to raise considerably the rotation of ethyl tartrate or similar substance, the influence of rise of temperature is to diminish the rotation of such a solution. This is the case, for instance, with dilute solutions of ethyl tartrate in water (Trans., 1901, **79**, 172; 1904, **85**, 1129) and in naphthalene * (Trans., 1902, **81**, 1139), and the same behaviour is shown by methyl tartrate and *n*-propyl tartrate in water (Trans., 1904, **85**, 1127, 1131). A somewhat similar behaviour is shown by dilute aqueous solutions of methyl-, ethyl-, and *n*-propyl-potassium tartrate, in which cases the specific rotation on heating at first increases to reach a maximum value and then diminishes again (Trans., 1904, **85**, 1121, 1123, 1125). We therefore suspected that, since the rotation of dilute solutions of ethyl tartrate in α-bromonaphthalene is so high, a maximum should occur in the temperature-rotation curve at a comparatively low temperature. The $p=2$ solution was therefore examined throughout a greater range of temperature than the others. Its rotation increased rapidly at first, but gradually more slowly, and passed through a maximum value of +29·6° at a temperature of 94°. The occurrence of such temperatures of maximum rotation is of very considerable interest, and further examples will be discussed in a future paper.

EXPERIMENTAL.

Ethyl Tartrate in Chlorobenzene.

The chlorobenzene boiled at 44·8° under a pressure of 30 mm. (oil-bath, 112°):

I. $p=3{\cdot}8059$.

$t°$ …………………	13·8°	17·4°	33·6°	40·0°	43·7°
$\alpha_D^{t°}$ (400 mm.)……	+1·872	1·955	2·275	2·391	2·450
$[\alpha]_D^{t°}$ ……………	+11·02	11·55	13·65	14·45	14·86

---

* In this case, diminution of the observed rotation was detected in a $p=10$ solution, but the specific solution showed a slight increase between 70° and 100°. At a higher temperature, the specific rotation also would doubtless have commenced to decrease.

Ethyl Tartrate in Chlorobenzene (continued).

II. $p = 10·0073$.

$t°$	11·3°	21·7°	32·0°	40·1°	47·8°	56·0°	100·0°
$\alpha_D^{t°}$(249·6 mm.)	+2·453	2·893	3·292	3·537	3·742	3·93	4·408
$[\alpha]_D^{t°}$	+8·74	10·41	11·97	12·96	13·82	14·63	17·19

III. $p = 24·9956$.

$t°$	13·0°	24·8°	38·8°	44·6°	59·3°	68·7°	100·0°
α_D^{t}(249·6 mm.)	+4·783	6·098	7·378	7·782	8·728	9·192	10·167
$[\alpha]_D^{t°}$	+6·75	8·78	10·68	11·52	12·87	13·71	15·66

IV. $p = 47·469$.

t	9·1°	13·1°	21·9°	37·9°	46·5°	57·3°	67·2°	100·0°
$\alpha_D^{t°}$ (100 mm.)...	+2·969	3·252	3·93	5·029	5·534	6·054	6·415	7·315
$[\alpha]_D^{t°}$...............	+5·39	5·92	7·22	9·37	10·40	11·49	12·29	14·49

V. $p = 75·345$.

$t°$......................	13·0°	22·0°	38·6°	55·5°	66·6°
$\alpha_D^{t°}$ (100 mm.)	+5·463	6·476	8·067	9·26	9·9
$[\alpha]_D^{t°}$	+6·11	7·31	9·24	10·77	11·64

Densities determined :

Solvent.		I.		II.		III.	
t°.	*d.*	*t°.*	*d.*	*t°.*	*d.*	*t°.*	*d.*
17·05°	1·10974	18·5°	1·11071	15·0°	1·12025	14·7°	1·13432
24·12	1·10215	24·25	1·10451	39·3	1·09382	36·0	1·11108
38·53	1·08650	31·87	1·09622	68·1	1·0622	63·2	1·0812
				99·0	1·0278	99·0	1·0415

IV.		V.	
t°.	*d.*	*t°.*	*d.*
17·9°	1·15180	18·8°	1·1797
36·3	1·13223	24·91	1·1732
65·5	1·1013	49·5	1·1472
101·3	1·0619		

Ethyl Tartrate in Bromobenzene.

The bromobenzene boiled at 43° under a pressure of 18 mm.:

I. $p = 9·93184$.

$t°$	11·0°	14·8°	24·0°	39·6°	47·0°	52·0°	100·0°
$\alpha_D^{t°}$ (249·6 mm.).	+2·91	3·127	3·705	4·402	4·66	4·84	5·725
$[\alpha]_D^{t°}$	+7·99	8·62	10·29	12·41	13·22	13·8	17·09

II. $p = 24·94$.

$t°$..................	9·6°	13·2°	18·0°	24·0°	37·7°	45·5°	55·3°	62·5°	100·4°
$\alpha_D^{t°}$ (249·6 mm.)	+5·439	5·97	6·655	7·354	8·859	9·574	10·32	10·838	12·584
$[\alpha]_D^{t°}$..............	+6·17	6·79	7·6	8·44	10·30	11·21	12·19	12·89	15·51

Ethyl Tartrate in Bromobenzene (continued).

III. $p = 47·967$.

t°	10·4°	13·0°	23·1°	41·2°	48·3°	56·2°	62·0°	100·3°
$\alpha_D^{t^\circ}$ (100 mm.)	+3·686	3·895	4·778	6·095	6·523	6·915	7·176	8·51
$[\alpha]_D^{t}$	+5·70	6·04	7·48	9·69	10·44	11·15	11·63	14·31

Densities determined :

Solvent.		I.		II.		III.	
t°.	*d.*	t°.	*d.*	t°.	*d.*	t°.	*d.*
14·3	1·50188	18·6	1·45914	19·4	1·4048	19·1	1·33699
42·8	1·46425	36·1	1·43590	38·0	1·3820	38·5	1·31434
58·6	1·44313	59·0	1·4059	61·6	1·352	61·0	1·2875
100·6	1·3862	100·6	1·3508	100·8	1·302	101·0	1·2392

Ethyl Tartrate in Iodobenzene.

The iodobenzene boiled at 69° under a pressure of 15 mm. (oil-bath, 110°) :

I. $p = 10·6375$.

t°	24·2°	40·1°	51·1°
$\alpha_D^{t^\circ}$ (170 mm.)	+3·05	3·62	4·04
$[\alpha]_D^{t^\circ}$	+9·78	11·77	13·26

II. $p = 24·9011$.

t°	16·8°	21·1°	36·4°	52·4°
$\alpha_D^{t^\circ}$ (70 mm.)	+2·21	2·35	2·88	3·36
$[\alpha]_D^{t^\circ}$	+7·83	8·36	10·38	12·29

III. $p = 49·8182$.

t°.....................	13·6°	26·4°	40·4°	51·5°	59·9°
$\alpha_D^{t^\circ}$ (70 mm.)	+3·65	4·45	5·12	5·61	5·94
$[\alpha]_D^{t^\circ}$..................	+7·19	8·86	10·33	11·43	12·18

IV. $p = 75·2983$.

t°	15·6°	21·6°	33·5°	45·5°
$\alpha_D^{t^\circ}$ (70 mm.)	+5·19	5·55	6·37	7·12
$[\alpha]_D^{t^\circ}$	+7·48	8·03	9·32	10·53

Densities determined :

Solvent.		I.		II.		III.		IV.	
t°.	*d.*	t°.	*d.*	t°.	*d.*	t°.	*d.*	t°.	*d.*
19·5°	1·83257	18·85°	1·73208	19·5°	1·61552	18·3°	1·45079	19·25°	1·31392
24·8	1·82363	24·1	1·72429	24·5	1·60846	24·15	1·44344	25·05	1·30724
31·25	1·8138	34·3	1·7090	29·6	1·6011	35·75	1·4288	36·2	1·2948
38·5	1·8027	51·6	1·6832	38·9	1·5881	53·2	1·4069	53·7	1·2749
				50·6	1·5716				

Ethyl Tartrate in p-*Dichlorobenzene*:*

$p = 5·002$.

t°	50·8°	55·6°	60·0°†	63·6°	72°	79·3°	97·0°
$[\alpha]_D^{t}$	+6·78	7·44	8·05	8·53	9·44	10·23	11·85

$p = 40·01$.

t°	53·7°	60·0°†	63·4°	72·4°	99·0°
$[\alpha]_D^{t}$	+6·62	7·4	7·8	8·82	11·18

$p = 60·01$.

t°	52·7°	57·0°	60·0°†	66·0°	75·0°	89·7°
$[\alpha]_D^{t}$	+7·77	8·35	8·7	9·37	10·25	11·5

Ethyl Tartrate in α-Bromonaphthalene.

The α-bromonaphthalene boiled at 139° under 16 mm. pressure (oil-bath, 166°):

I. $p = 2·07933$.

t°	16·9°	25·2°	38·5°	52·1°	79·0°	110·5°
α_D^{t} (160 mm.)	+1·003	1·07	1·182	1·276	1·38	1·345
$[\alpha]_D^{t}$	+20·36	21·83	24·34	24·51	29·2	29·05

II. $p = 4·99697$.

t°	15·0°	33·5°	47·2°	59·3°
α_D^{t} (160 mm.)	+1·806	2·318	2·58	2·76
$[\alpha]_D^{t}$	+15·3	19·9	22·3	24·1

III. $p = 20·2601$.

Only examined for density and solution-volume.

IV. $p = 20·37$.

t°	19·4°	24·3°
α_D^{t} (100 mm.)	+3·25	3·51
$[\alpha]_D^{t}$	+11·8	12·22

V. $p = 49·6882$.

t°	13·5°	20·0°	31·0°	42·5°	52·1°
α_D^{t} (100 mm.)	+5·535	6·17	7·216	8·08	8·703
$[\alpha]_D^{t}$	+8·31	9·32	11·04	12·51	13·62

Densities determined:

Solvent.		I.		II.		III.	
t°.	d.	t°.	d.	t°.	d.	t°.	d.
18·55°	1·49225	19·8°	1·47853	18·95°	1·47269	18·65°	1·42089
20·75	1·49006	22·8	1·47549	20·95	1·47069	20·75	1·41853
23·0	1·48777	31·3	1·46697	24·3	1·46727	24·25	1·41491

IV.		V.	
t°.	d.	t°.	d.
20·15°	1·414	18·7°	1·33226
		20·55	1·33026
		23·6	1·3270

---

* Unfortunately, the manuscript book containing the original data for these solutions has been mislaid, so that the observed rotations and densities cannot be given. As we had a note of the specific rotations at various temperatures, we did not consider it necessary to repeat the experiments in order to obtain values for the missing constants.

† Interpolated.

Molecular Solution-volume and Specific Rotation at 20° of Ethyl Tartrate in Various Solvents.

Molecular Volume of Ethyl Tartrate at 20° = 170·9 c.c.; $[\alpha]_D^{20°}$ +7·76°.

In several cases, two or more different samples of solvent were used. In such instances, the density for $p = 0$ appears more than once. The numbers immediately following each 0 represent solutions made up with that specimen of solvent. We have not attempted to estimate values for M.S.V.$^{20°}$ at infinite dilution.

Solvent.	p.	d 20°/4°.	M.S.V.$^{20°}$. c.c.	$[\alpha]_D^{20°}$.
Chlorobenzene	0	1·10674	—	+13·3°
	5·49034	1·11081	173·71	—
	0	1·10657	—	13·3
	3·8059	1·10909	175·05	11·87
	10·0073	1·11481	172·41	10·14
	24·996	1·12854	171·67	8·00
	47·47	1·14957	171·45	6·98
	75·345	1·1784	171·1	6·99
Bromobenzene	0	1·49447	—	11·7
	4·99987	1·47496	174·91	—
	0	1·49434	—	11·7
	9·93184	1·45728	173·15	9·6
	24·94	—	—	7·86
	47·967	1·33594	171·9	7·03
Iodobenzene	0	1·83173	—	11·0
	10·6375	1·73038	174·38	9·2
	24·9011	1·61482	173·12	8·2
	49·8182	1·44856	172·17	8·0
	75·2983	1·3131	171·46	7·9
	0	1·83174	—	11·0
	4·96374	1·78225	175·38	—
α-Bromonaphthalene ...	0	1·48651	—	26·0
	2·07933	1·47833	175·46	20·9
	0	1·49081	—	26·0
	4·99697	1·47164	174·2	16·6
	20·2601	1·41937	172·5	—
	20·37	—	—	11·4
	49·6882	1·33085	171·6	9·32

It gives us pleasure, in conclusion, to acknowledge our indebtedness to the Research Fund Committee of the Chemical Society for a grant which partly defrayed the expenses of this investigation.

THE UNIVERSITY,
GLASGOW.

LXXXIX.—*Acetylketen: a Polymeride of Keten.*

By Frances Chick and Norman Thomas Mortimer Wilsmore.

It has been already stated (*Nature*, 1907, **75**, 510; Trans., 1907, **91**, 1938) that keten, both in the liquid and the gaseous states, condenses on standing at the ordinary temperature to form a pungent-smelling brown liquid. This brown liquid has now been found to contain a new substance, which, as we hope to show in in the present paper, is in all probability *acetylketen*, having the formula

$$CH_3\cdot CO\cdot CH\colon CO,$$

and, consequently, standing in the same relation to acetoacetic acid as keten does to acetic acid.

As was to be expected, this condensation of keten takes place the more readily the purer and the more concentrated the keten is, and is therefore most conveniently brought about by allowing liquefied keten under pressure gradually to attain the temperature of the room. To carry out the operation, the crude keten is first roughly fractionated in the receiver of the apparatus, already described (Trans., *loc. cit.*), in order to expel the bulk of the more volatile impurities. As soon as the boiling point has risen to −70° to −65°, the taps are closed, and the keten is frozen by means of liquid air. The receiver is then connected, on the one hand, to an exhaust pump and, on the other, to a manometer and to a thick-walled glass tube, closed at one end, and drawn off to a thick-walled capillary at the other. After the whole apparatus has been exhausted, the connexion to the pump is closed, and the keten is distilled over by removing the liquid air-bath from the receiver and applying it to the thick-walled tube. When all the keten has passed over, the thick-walled tube is sealed off.

It was mentioned in the previous paper that the spontaneous condensation of keten was accompanied by considerable evolution of heat. This was noticed first on handling one of the tubes about half an hour after it had been sealed up, when the end of the tube containing the liquid was found to be much too hot to hold. In order to follow the reaction more carefully, a sealed tube containing about 7 c.c. of liquid keten was placed, along with a thermometer, in a wide glass tube containing 50 c.c. of alcohol, which had been previously cooled to about −60°. The apparatus was placed in the open air, and was observed from a distance by means of a telescope. The keten remained colourless until the temperature of the bath had risen to 0°, when it began slowly to turn brown. The reaction then went on with increasing rapidity, and the temperature of the bath gradually rose to 21°, remained at that point for about a quarter of an hour, and then slowly fell. The temperature of the air outside varied, meanwhile, between 10° and 7°. The reaction appeared to be complete after about three-quarters of an hour from the time when the keten began to turn brown. A second similar tube was placed in an air jacket and was observed as before. In this case a violent reaction, lasting for nearly five minutes, took place soon after the liquid began to turn brown. The heat of the reaction is therefore considerable. A quantitative determination of it by means of an ice calorimeter is contemplated.

On distilling the brown liquid, it was found to consist partly of a colourless liquid, which passed over between 125° and 127°, and partly of a brown residue, which is now being further examined. The yield of the colourless liquid was not very large, about 5 grams being obtained from 200 grams of acetic anhydride. On redistilling the colourless liquid under a pressure of 760 mm., it boiled at 126—127° with slight decomposition, a portion being always converted into some of the brown solid; but it could be distilled under reduced pressure (50—100 mm.) without change.

For analysis, the substance was weighed in a small stoppered bottle of hard glass, which was opened and placed in the boat as the latter was being pushed into the combustion tube.* The vapour density was determined by means of the Hofmann apparatus, using freshly-distilled *m*-xylene for the vapour jacket. In calculating the net pressure, allowance was made for the temperature of the mercury column, and for the vapour pressure of the mercury in the tube. Owing to the tendency of the vapour to polymerise, the result is rather high:

0·1419 gave 0·2938 CO_2 and 0·0614 H_2O. C = 56·5; H = 4·8.
0·1118 „ 0·2331 CO_2 „ 0·0500 H_2O. C = 56·9; H = 5·0.
0·0971 „ 71·4 c.c. at 139·3° and 409 mm. M.W. = 85·8.
0·4034 in 18·20 benzene gave a depression of 1·315°. M.W. = 84·3.
$C_4H_4O_2$ requires C = 57·1; H = 4·8 per cent. M.W. = 84·0.

The substance is therefore formed by the union of two molecules of keten.

The liquid dissolved slowly on shaking with cold water, forming a strongly acid solution, which gave a deep violet colour with ferric chloride. On heating the aqueous solution, carbon dioxide and acetone were formed, the latter being recognised by means of the iodoform reaction, the alkaline mercuric chloride test, and the formation of the crystalline compound with benzaldehyde. Hydrogen chloride facilitated the dissolution and decomposition. On warming the substance or its aqueous solution with aqueous alkalis, it was decomposed, acetates being formed. The substance therefore combines with water to form acetoacetic acid.

---

* The liquid was too volatile to weigh in the boat, and when placed in the usual bulb-tube the brown solid formed in the capillary on heating could not be completely burnt.

The liquid was found to react with aniline with great energy; in fact, if the aniline was added too quickly, the mixture boiled. A crystalline substance was produced, which, after recrystallisation from alcohol, proved to be acetoacetanilide, melting at 84°. This was confirmed by heating a portion with excess of aniline, when carbanilide (m. p. 235°) was formed.

All the above reactions may be satisfactorily explained on the assumption that the new body is *acetylketen*. Thus with water we have:

$$CH_3\cdot CO\cdot CH\colon CO + H_2O = CH_3\cdot CO\cdot CH_2\cdot CO_2H,$$

with alkalis:

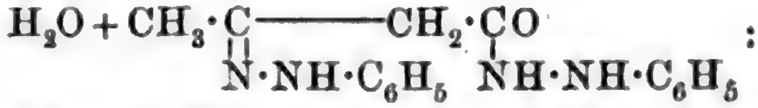
$$CH_3\cdot CO\cdot CH\colon CO + Ba(OH)_2 = Ba(C_2H_3O_2)_2,$$

and with aniline:

$$CH_3\cdot CO\cdot CH\colon CO + C_6H_5\cdot NH_2 = CH_3\cdot CO\cdot CH_2\cdot CO\cdot NH\cdot C_6H_5.$$

Acetylketen in benzene solution reacts with two molecular proportions of phenylhydrazine, yielding a substance which crystallised from alcohol or benzene in colourless plates melting with slight decomposition at 152°—153°. Analysis showed that this substance had the composition of a *phenylhydrazone-phenylhydrazide*. It is probably formed according to the equation:

$$CH_3\cdot CO\cdot CH\colon CO + 2C_6H_5\cdot N_2H_3 =$$



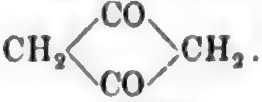
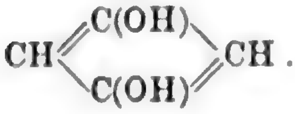
$$H_2O + CH_3\cdot\underset{\overset{\|}{N\cdot NH\cdot C_6H_5}}{C}\text{———}CH_2\cdot\underset{\overset{|}{NH\cdot NH\cdot C_6H_5}}{CO}\quad :$$

0·1156 gave 0·2877 CO_2 and 0·0677 H_2O. C = 67·9; H = 6·5.
0·1214 „ 0·3022 CO_2 „ 0·0705 H_2O. C = 67·9; H = 6·5.
0·1114 „ 19·67 c.c. moist nitrogen at 18° and 754 mm. N = 20·1.
0·1775 in 16·98 benzene gave an elevation of 0·095°. M.W. = 288.
$C_{16}H_{18}ON_4$ requires C = 68·1; H = 6·4; N = 19·9 per cent. M.W = 282.

The substance dissolved readily in dilute hydrochloric acid, forming a very soluble hydrochloride, which gave a well-defined *platinichloride*.

Acetylketen differs markedly from keten in that it does not appear to react either with alcohols or with phenols, and this fact gave rise to the suggestion that it might be after all not a true keten, but an isomeride, such as diketotetramethylene.

To test this point the molecular refraction was determined, and the result was compared with the values calculated for the various isomeric formulæ from Conrady's numbers for the atomic refractions for sodium light (*Zeitsch. physikal. Chem.*, 1889, **3**, 210). The pyknometer contained 0·7433 gram of water weighed in air at 18°, 0·8143 gram of acetylketen at 18°, and 0·8118 gram at 23°; reducing to the vacuum and to the density of water at 4°, the density of acetylketen was accordingly $d_{18^\circ} = 1·0939$ and $d_{23^\circ} = 1·0905$. The refractive index, measured with a Pulfrich apparatus at 23°, using sodium light, was $n_D = 1·4342$, which from the Lorentz formula gives M.R. = 20·075. The calculated values are:

	M.R.
$CH_3\cdot CO\cdot CH:CO$	20·489
$CH_2:C(OH)\cdot CH:CO$	21·430
	18·782
	20·664

Thus the acetylketen formula appears, according to this test also, to be the most probable, the only other formula which approaches it being that of the otherwise highly unlikely phenolic form of diketotetramethylene. There is, nevertheless, still a considerable difference between the calculated and the observed value for acetylketen, but, perhaps, this may be due to the oxygen in the terminal CO group having a lower atomic refraction than "aldehydic" oxygen in general. We hope to test this hypothesis shortly by determining the molecular refraction of keten itself.

As already mentioned, acetylketen is a colourless liquid at the ordinary temperature. On cooling sufficiently, it freezes to a white solid, which melts at −7° to −6°. It has an extremely pungent smell, differing entirely from that of keten, and suggestive at the same time of acetic anhydride and of acrolein. Its vapour attacks the eyes and the mucus membranes, but, like keten, it does not appear to leave any unpleasant after-effects. On standing at the ordinary temperature, even in absence of air, it gradually turns brownish-yellow. The change is, however, less rapid in Jena than in soda glass, and is in any case extremely slow at 0°. It would seem not to proceed very far even at the ordinary temperature, since a bomb tube which had been left sealed up for several months gave, when opened, practically the same yield as tubes freshly prepared. The boiling point, density, and refractive index have been already given. The dielectric constant has been measured for us by Dr. A. W. Stewart by means of the Drude apparatus, the value 16—17, or practically the same as that of acetoacetic ester, being obtained. The absorption spectrum of acetylketen was photographed by Mr. H. E. Watson, using solutions in dry ether and in alcohol up to 0·1*N*.

There was no absorption band, but a small general absorption in the ultra-violet resembling that produced by acetoacetic ester.

Acetylketen is readily miscible with all the usual organic solvents. It reacts violently with pyridine, forming a brown substance apparently identical with that which we have observed to be formed by the action of keten on pyridine. The pyridine seems to act merely as a catalytic agent, since it could be readily washed out from the mixture, leaving a residue free from nitrogen. The reaction proceeded much more slowly in benzene solution, the acetylketen being then almost entirely converted into dehydracetic acid, which, after crystallisation from alcohol and light petroleum, melted at 108·5°. On the other hand, acetylketen reacts slowly with quinoline, yielding a sparingly soluble, crystalline substance melting with decomposition at 231°, which, however, does not contain nitrogen. With sodium ethoxide in dry alcohol, acetylketen forms chiefly sodium ethylacetoacetate. This, on treatment with hydrogen chloride, gave carbon dioxide and a ketone, which was evidently methyl propyl ketone. Hydroxylamine hydrochloride has no action on acetylketen, but the latter combines readily with the free base in alcoholic solution. Hantzsch's methylisooxazolone was, however, not produced, but a very soluble, readily oxidisable, crystalline substance was obtained on evaporation.

We are continuing the investigation both of keten and of acetylketen, and we propose to study especially the action of Grignard's reagent on these substances.

Our thanks are due to Mr. H. T. Clarke, who kindly assisted in the carrying out of several of the experiments.

UNIVERSITY COLLEGE,
UNIVERSITY OF LONDON.

XC.—*The Condensation of Benzoin with Methyl Alcohol.*

By JAMES COLQUHOUN IRVINE, D.Sc., Ph.D., and DAVID McNICOLL, M.A., B.Sc.

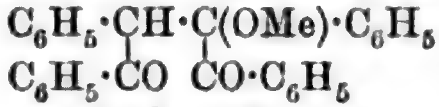
IN a previous paper (Trans., 1907, **91**, 1391), it has been pointed out that, although a good yield of benzoin methyl ether is obtained from benzoin by the application of Fischer's process, two other compounds are produced simultaneously which are not apparently intermediate products in the methylation, but result from definite side-reactions.

So far as preliminary experiments showed, one of these compounds (m. p. 185°) was produced by the union of one molecule of benzoin with one of benzoin methyl ether through loss of one molecule of water; the second compound (m. p. 285°) had the same analytical composition as benzoin methyl ether, but possessed a molecular weight twice as great, and was regarded as a tetramethylene derivative. The formation of such a compound suggested that benzoin methyl ether had undergone condensation in a manner resembling in some ways the "benzoin" condensation, and this view was apparently supported by evidence which showed that the presence of nitrogen compounds seemed to favour the production of the substance, presumably by catalytic action. We were thus led to make a more detailed study of the two condensation compounds and of their mode of formation.

Attempts to synthesise the two compounds from benzoin methyl ether gave no positive result, our experiments indicating that both substances are in fact produced directly from benzoin, independently of the methylation of the latter to benzoin methyl ether. Thus, when benzoin methyl ether was subjected to the action of methyl alcohol containing varying proportions of hydrogen chloride, only traces of the sparingly soluble products were formed. Negative res lts were also obtained when hydrogen cyanide and benzaldehyde were added to a similar mixture. Moreover, the yield of the two compounds was not appreciably increased by carrying out Fischer's process with a methyl-alcoholic solution of benzoin to which potassium cyanide and benzaldehyde had been added, so that apparently the secondary reactions are not affected, as was suggested in a previous paper, by the presence of nitriles.

Although throughout all our work we have used Kahlbaum's "Aceton frei" methyl alcohol, we considered it advisable, in view of the ready condensation of benzil with acetone, to ascertain if the latter played any part in the reaction and thus account for the somewhat variable yields of the desired products which we have obtained in different preparations. It was found, however, that the addition of acetone, either in traces or in molecular proportions, not only failed to lead to any noticeable increase in the amount of the by-products, but in some cases diminished the yields, owing to the formation of mesityl oxide. The addition of benzil or benzoic acid to the above mixture also proved fruitless.

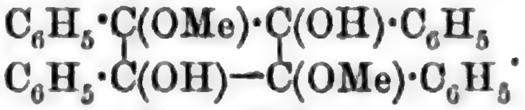
We conclude, therefore, that the two compounds under examination are formed in a reaction in which benzoin, methyl alcohol, and hydrogen chloride alone play a part, and, in preparing the necessary material, dry hydrogen chloride was passed into a solution of pure benzoin in pure methyl alcohol. The joint yield of the two compounds was somewhat improved by introducing the acid as rapidly as possible and by carrying out the preparation at 10°, instead of at 40—50° as in previous cases, but in no instance did the total yield exceed 37 per cent. of the benzoin used. The first crops to separate consisted of the compound of lower melting point in a state of purity; later crops consisted of mixtures of both substances, and finally the compound melting at 285° was alone produced. This is explained by the fact that the compound of lower melting point is capable of uniting with a molecule of methyl alcohol under the conditions of the reaction, and is thus converted into the compound melting at 285°. The constitution of these substances was in the previous research left undecided, but the formulæ suggested were respectively:



$$\begin{array}{l} C_6H_5\cdot CH\cdot C(OMe)\cdot C_6H_5 \\ C_6H_5\cdot CO\quad CO\cdot C_6H_5 \end{array}$$

(M. p. 185°.)

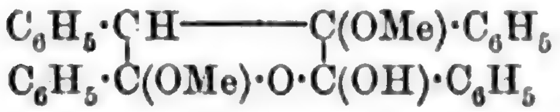
and



$$\begin{array}{l} C_6H_5\cdot C(OMe)\cdot C(OH)\cdot C_6H_5 \\ C_6H_5\cdot C(OH)-C(OMe)\cdot C_6H_5 \end{array}.$$

(M. p. 285°.)

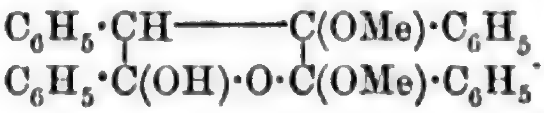
The first-mentioned formula is no longer tenable, no indication being obtained of the presence of ketonic groups. Moreover, the reaction mentioned above, in which the compound of lower melting point is converted into the other by the addition of methyl alcohol, is not readily explained, except on the assumption that both substances possess a similar structure. That this view is correct was shown by the action of acetic anhydride containing sulphuric acid. Both compounds, although quite unaffected by either acetic anhydride or acetyl chloride, reacted readily with the stronger reagent in the cold and gave identical products, one of which was readily recognised as acicular dibenzoylstilbene. This at once points to the fact that both the substances under examination are furan derivatives, and both formulæ must therefore be abandoned. A second product of the acetylation had the composition $C_{34}H_{30}O_7$, and contained three acetyl groups, the methoxyl groups having been eliminated during the reaction. The evidence thus obtained points to the following alternative formulæ for the compound melting at 285°:



$$\begin{array}{l} C_6H_5\cdot CH\text{———}C(OMe)\cdot C_6H_5 \\ C_6H_5\cdot C(OMe)\cdot O\cdot C(OH)\cdot C_6H_5 \end{array}$$

(I.)

or

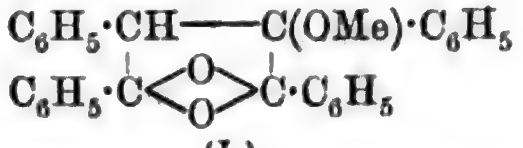


$$\begin{array}{l} C_6H_5\cdot CH\text{———}C(OMe)\cdot C_6H_5 \\ C_6H_5\cdot C(OH)\cdot O\cdot C(OMe)\cdot C_6H_5 \end{array}.$$

(II.)

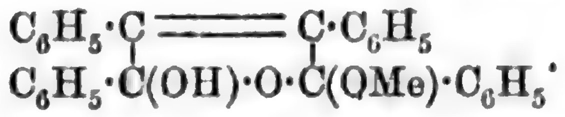
The action of acetic anhydride and sulphuric acid may thus be regarded as acetylation of two methoxyl groups and one hydroxyl group, a reaction which involves the removal of two molecules of methyl alcohol. The above general structure was also supported by the observation that acetic anhydride and sulphuric acid decomposed the triacetyl derivative at 100° with the formation of dibenzoylstilbene, and that hydrogen iodide reduced the original substance to tetraphenylfuran. We believe formula I to be the more probable structure, as it involves the symmetrical addition of methyl alcohol to dibenzoylstilbene, but no indication could be obtained of the presence of the hydroxyl group further than the formation of a triacetyl derivative from the compound, which previous analyses had shown to contain two methoxyl groups. The compound is therefore 2-*hydroxy*-3 : 5-*dimethoxytetraphenyltetrahydrofuran.*

The structure of the compound melting at 185° can be arrived at by considering the alternative methods of removing one molecule of methyl alcohol from the substance just mentioned. Two possibilities exist, namely :



(I.)

and



$$\begin{array}{l} C_6H_5\cdot C = C\cdot C_6H_5 \\ C_6H_5\cdot C(OH)\cdot O\cdot C(OMe)\cdot C_6H_5 \end{array}$$

(II.)

Either formula would explain the property of addition of one molecule of methyl alcohol by the action of alcoholic hydrogen chloride, or the formation of dibenzoylstilbene when treated with acetic anhydride and sulphuric acid. As the substance does not give the reactions of a hydroxy-compound and forms no additive compound with bromine, we believe it to have the constitution I. It is therefore *αβ-dibenzoyl-α-methoxydibenzyl.**

It seems probable that the formation of these by-products arises in the first instance from the condensation of two molecules of benzoin to form dibenzoylstilbene (*Ber.*, 1877, **4**, 337), which then unites with two molecules of methyl alcohol in two successive stages to form αβ-dibenzoyl-α-methoxydibenzyl and, finally, 2-hydroxy-3 : 5-dimethoxytetraphenyltetrahydrofuran. It is of course well known (*Chem. Centr.*, 1867, 373) that concentrated hydrochloric acid reduces dibenzoylstilbene to tetraphenylfuran, but we find that, if the gas is passed slowly into a dilute methyl-alcoholic solution of the former, it is converted in the first place into a mixture of the two compounds under examination ; prolonged action of the acid gives a mixture of tetraphenylfuran and 2-hydroxy-3 : 5-dimethoxytetraphenyltetrahydrofuran.

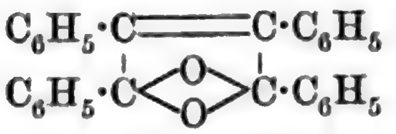
The complete reaction between methyl alcohol and benzoin in presence of hydrogen chloride is therefore expressed in the following scheme :

$$\begin{tikzcd} & \text{Benzoin methyl ether.} & & \\ \text{Benzoin} \arrow[ur] \arrow[r] \arrow[dr] & \text{Dibenzoylstilbene} \arrow[r] & \alpha\beta\text{-dibenzoyl-}\alpha\text{-methoxydibenzyl} \arrow[r] & \text{2-hydroxy-3 : 5-dimethoxytetraphenyltetrahydrofuran.} \\ & \text{Benzil.} & & \end{tikzcd}$$

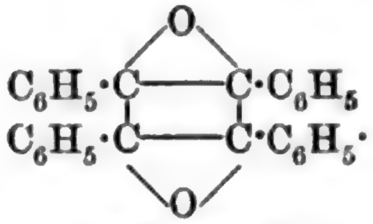
Our results throw some light on the alternative formulæ suggested for dibenzoylstilbene and tetraphenylfuran. Zinin's formula for the former has been questioned by Japp and Tingle (Trans., 1897, **71**, 1139; *Ber.*, 1888, **21**, 2934) and also by Dorn (*Annalen*, 1870, **153**, 358). According to these investigators, the structure of dibenzoylstilbene is represented by:

---

* Although there seems no reasonable doubt that the compound here described is cyclic, we have, for the sake of uniformity, referred to it as a dibenzoyl derivative, thus bringing it into line with dibenzoylcinnamene and dibenzoylstilbene.

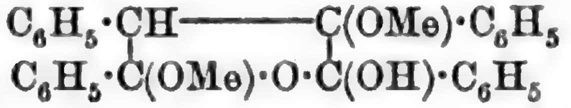


(Japp's formula.)



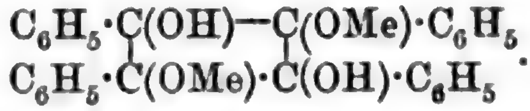
(Dorn's formula.)

The addition of two molecules of methyl alcohol can be conveniently represented by the use of either formula and results in the following alternative structures for hydroxydimethoxytetraphenyltetrahydrofuran:



$$\begin{array}{l} C_6H_5\cdot CH\text{———}C(OMe)\cdot C_6H_5 \\ C_6H_5\cdot C(OMe)\cdot O\cdot C(OH)\cdot C_6H_5 \end{array}$$

or



$$\begin{array}{l} C_6H_5\cdot C(OH)\text{—}C(OMe)\cdot C_6H_5 \\ C_6H_5\cdot C(OMe)\cdot C(OH)\cdot C_6H_5 \end{array}.$$

The formation of a triacetyl derivative excludes the constitution deduced from Dorn's formula, and we have therefore adopted Japp's structure throughout.

EXPERIMENTAL.

Condensation of Benzoin with Methyl Alcohol.

The best yields of the two furan derivatives were obtained by rapidly passing dry hydrogen chloride into a methyl-alcoholic solution of benzoin cooled to 10°. At this temperature, benzoin requires twenty-five times its weight of alcohol to effect complete solution. The separation of the sparingly soluble condensation products began when the solution contained about 15 per cent. of hydrogen chloride, and ceased when the disappearance of any action on Fehling's solution indicated that no free benzoin was present. The solution was filtered at intervals, and finally allowed to stand in the cold for twenty-four hours. The first and last crops to separate melted sharply at 185° and 285° respectively, intermediate crops being mixtures of the two compounds, which were separated as described in a previous paper (*loc. cit.*). The relative amount of the two substances formed depends on a number of conditions, and seems to be determined by the temperature of the solution, the rate of saturation with hydrogen chloride, and the intervals of time which elapse between the filtration of the different crops. 2-Hydroxy-3:5-dimethoxytetraphenyltetrahydrofuran constituted the sole product when the mixed crops were not removed, but were allowed to stand in contact with the acid mother liquor for some days.

An alternative method of preparation consists in mixing benzoin with eight times its weight of methyl alcohol, saturating the latter with hydrogen chloride, and allowing to stand in the cold for several weeks. Using these proportions, the bulk of the benzoin remains undissolved, but is slowly converted into hydroxydimethoxytetraphenyltetrahydrofuran, the yield of which amounted to 20 per cent. of the benzoin used.

Action of Acetic Anhydride and Sulphuric Acid on 2-Hydroxy-3 : 5-dimethoxytetraphenyltetrahydrofuran.

On adding 5 grams of the compound to 180 c.c. of acetic anhydride containing a few drops of concentrated sulphuric acid, an intense violet solution was obtained. On standing at the temperature of the room, a very characteristic series of colour changes were observed, the liquid finally becoming crimson and displaying well-marked fluorescence. A crop of small prisms weighing 3·7 grams rapidly separated, which, after three recrystallisations from a mixture of benzene and methyl alcohol, melted sharply at 292° ; the acetic anhydride mother liquor, on concentration at 50° under 15 mm. pressure, gave a bright yellow, crystalline product, which, after recrystallisation from benzene, melted at 210—211°.

The first of these products proved to be a *triacetyl* derivative.

Found, $C=74\cdot29$; $H=5\cdot32$; $CH_3\cdot CO=24\cdot34$.

$C_{28}H_{21}O_4(CH_3\cdot CO)_3$ requires $C=74\cdot18$; $H=5\cdot45$; $CH_3\cdot CO=23\cdot45$ per cent.

A Zeisel estimation gave a negative result, showing that the methoxyl groups had been completely removed, and a determination of the molecular weight in benzene solution by the cryoscopic method gave the value 511 ($C_{34}H_{30}O_7$ requires 550). The compound was insoluble in water, sparingly soluble in alcohol, but readily so in benzene. It behaved as a saturated substance towards bromine, and was quantitatively hydrolysed by boiling with *N*/2-alcoholic potassium hydroxide. When gently warmed with acetic anhydride containing a little sulphuric acid, it was completely converted into dibenzoylstilbene.

The yellow compound referred to above (m. p. 210—211°), which was contained in the acetic anhydride mother liquor, was proved by analyses and conversion into tetraphenylfuran to be dibenzoylstilbene. The melting point quoted by Zinin (220°) appears to be too high, as our experience agrees with that of Japp and Klingemann (Trans., 1890, **57**, 688), who state that they "could not, by any process of crystallisation, succeed in raising the melting point above 210—211°."

Action of Hydrogen Iodide.—Five grams of 2-hydroxy-3 : 5-dimethoxytetraphenyltetrahydrofuran were heated at 120° in the decomposition flask of a Zeisel apparatus with a large excess of hydriodic acid (sp. gr. 1·76) until the evolution of methyl iodide ceased. The liquid was neutralised with solid sodium carbonate, extracted with a large excess of ether, and the ethereal solution shaken with sodium thiosulphate solution until free from iodine. After standing over anhydrous sodium sulphate and removal of the solvent, a crystalline residue was obtained, from which deoxybenzoin and tetraphenylfuran were isolated and identified by conversion into deoxybenzoinoxime and dibenzoylstilbene respectively.

The reduction by Baeyer's method was carried out in an atmosphere of carbon dioxide, and gave a crystalline distillate. After drying on porous porcelain, the product was dissolved in boiling alcohol, when a crop of lustrous plates separated, melting at 124°, which were further identified as stilbene by conversion into the α-dibromide. The alcoholic mother liquor contained a quantity of deoxybenzoin. The reduction therefore resulted in molecular rupture.

On adding a solution of bromine in carbon disulphide to a similar solution of 2-hydroxy-3 : 5-dimethoxytetraphenyltetrahydrofuran, no reaction took place, and on evaporation of the solvent the original weight of substance was recovered unaltered. A negative result was also obtained in experiments in which a benzene solution of the compound was boiled with phosphorus pentachloride. There was no apparent reaction, and the unchanged substance was recovered. We have thus no direct indication of the presence of the hydroxyl group.

Reactions of αβ-Dibenzoyl-α-methoxydibenzyl.

All the reactions of this compound were carried out in the manner already described for 2-hydroxy-3 : 5-dimethoxytetraphenyltetrahydrofuran, and in most cases identical results were obtained. Thus a mixture of acetic anhydride and sulphuric acid converted it into the same triacetyl derivative, $C_{28}H_{21}O_4(CH_3{\cdot}CO)_3$, melting at 292°, and also into dibenzoylstilbene (m. p. 210—211°). When reduced with hydrogen iodide, a mixture of tetraphenylfuran and deoxybenzoin was obtained, and, when distilled with zinc dust, deoxybenzoin and stilbene were produced. Although soluble in excess of methyl iodide, the compound was recovered unchanged when this solution was boiled for twelve hours with silver oxide. By the action of bromine in carbon disulphide solution, a considerable quantity of hydrogen bromide was formed, with the result that molecular rupture ensued. On evaporation of the solvent and purification of the crystalline residue from alcohol, a compound crystallising in prismatic needles, melting at 110—112°, was obtained. As the substance was completely decomposed by alcoholic silver nitrate solution, it was evidently 2:2-dibromodeoxybenzoin.

Action of Methyl Alcohol and Hydrogen Chloride.

Some difficulty was experienced in carrying out this experiment, as at moderate temperatures very little of the compound remains dissolved in methyl alcohol, and thus very dilute solutions had to be used. On passing hydrogen chloride into such a solution, a white, crystalline precipitate gradually formed, which proved to be pure 2-hydroxy-3:5-dimethoxytetraphenyltetrahydrofuran. It was found necessary to keep the liquid thoroughly mixed during the solution of the gas, as otherwise benzil was formed in quantity, whilst the sparingly soluble precipitate was then found to contain tetraphenylfuran.

Synthesis of the Condensation Compounds rom Dibenzoylstilbene.

Seventy-five grams of benzoin were mixed with 90 c.c. of concentrated hydrochloric acid, and heated at 140° for ninety minutes. The crude product, when separated as usual from benzil, amounted to 20 grams, so that the method of prolonging the heating for eight hours (Japp and Klingemann, *loc. cit.*) seems to be unnecessary. The oxidation to dibenzoylstilbene was carried out by Zinin's method by the action of nitric acid in acetic acid solution.

As dibenzoylstilbene is very sparingly soluble in methyl alcohol, a very large bulk of the latter was required to effect complete solution, even at the boiling point. On passing dry hydrogen chloride into the boiling solution, white crystals separated, which, from the melting point, appeared to consist largely of tetraphenylfuran. The reaction was accordingly repeated at a lower temperature (30—40°). Under these conditions, part of the dibenzoylstilbene invariably separated in the crystalline form during the solution of the gas. The yellow solution subsequently became colourless, and the undissolved dibenzoylstilbene rapidly passed into solution. This was almost immediately followed by the separation of a microcrystalline, white powder, which was collected in separate crops from time to time. The first portions contained both 2-hydroxy-3:5-dimethoxytetraphenyltetrahydrofuran and $\alpha\beta$-dibenzoyl-α-methoxydibenzyl, mixed, however, with unaltered dibenzoylstilbene, which, although it retained its original melting point, was now quite white; the later crops, which were removed from the strongly acid mother liquors, consisted almost entirely of tetraphenylfuran.

The formation of the two condensation products by this method is important, as giving an index of their probable mode of formation, but is more tedious than the direct preparation from benzoin, and the yields are poorer.

We have already ascertained that, during the methylation of anisoin, reactions occur, similar to those described in the present paper, and we are therefore extending the investigation to other substituted benzoins.

In conclusion, we desire to express our indebtedness to the Carnegie Trust and to the University Court for research grants, and to thank Professor Purdie for his interest and advice.

Chemical Research Laboratory,
United College of St. Salvator and St. Leonard,
University of St. Andrews.

XCI.—*A New General Method of Preparing Diazonium Bromides.*

By Frederick Daniel Chattaway.

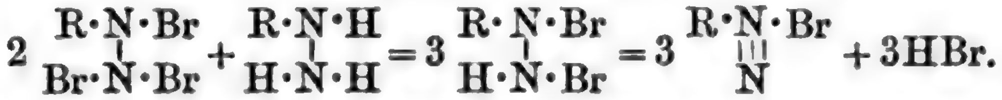
The more soluble of the diazonium salts cannot conveniently be separated from aqueous solution in a solid form by the device of adding alcohol and ether originally proposed by Griess (*Phil. Trans.*, 1864, **154**, 668), and are generally prepared by a method introduced by Knoevenagel (*Ber.*, 1890, **23**, 2994), in which a salt of the amine, suspended in alcohol, is diazotised by amyl nitrite.

The few diazonium bromides which have been described have been made by this method (Hantzsch, *Ber.*, 1895, **28**, 1748) or by the intramolecular rearrangement of bromo-substituted diazonium chlorides (Hantzsch and Smythe, *Ber.*, 1900, **33**, 505), or by the action of bromine on diazoamino-compounds, a reaction also discovered by Griess (*loc. cit.*, 672), who prepared benzenediazonium bromide by adding bromine to an ethereal solution of diazoaminobenzene; the diazonium bromide separated as a crystalline powder, whilst 2:4:6-tribromoaniline, which is formed at the same time, remained dissolved in the ether.

Although bromine quantitatively converts primary aromatic hydrazines into the corresponding diazonium bromides (Chattaway, Trans., 1908, **93**, 852), the reaction is not altogether convenient for preparing the solid salts, as, in order to prevent local heating consequent on the energetic action, a very low temperature has to be maintained if large quantities of the solvents are to be avoided.

A remarkably easy method of preparing these substances is, however, found in the reaction between primary aromatic hydrazines and the corresponding diazonium perbromides.

Primary aromatic hydrazines react quantitatively with the diazonium perbromides, producing diazonium bromides, thus:



$$2\begin{matrix} R\cdot N\cdot Br \\ | \\ Br\cdot N\cdot Br \end{matrix} + \begin{matrix} R\cdot N\cdot H \\ | \\ H\cdot N\cdot H \end{matrix} = 3\begin{matrix} R\cdot N\cdot Br \\ | \\ H\cdot N\cdot Br \end{matrix} = 3\begin{matrix} R\cdot N\cdot Br \\ ||| \\ N \end{matrix} + 3HBr.$$

As the diazonium perbromides are so easily obtained in the solid state by adding bromine to aqueous solutions of diazonium salts, and as they can be kept in a dry atmosphere for a long time without alteration and are comparatively safe to handle, the reaction affords a very convenient method for preparing diazonium bromides in the solid state.

For this purpose, it is only necessary to suspend the finely-powdered perbromide in anhydrous alcohol or acetic acid, and, after cooling, to add the calculated quantity of the corresponding hydrazine, also dissolved in the same solvent and cooled. The diazonium bromide either separates as a crystalline powder or can be made thus to separate by the addition of ether.

As the diazonium bromides are very deliquescent, care should be taken to avoid the presence of water in the solvents used, as otherwise, on the addition of ether, oily liquids separate, which are only brought into the crystalline state with difficulty. The reaction appears to be a general one.

Preparation of Benzenediazonium Bromide by the Interaction of Phenylhydrazine and Benzenediazonium Perbromide.

6·9 Grams of benzenediazonium perbromide, very finely powdered, were suspended in 30 c.c. of absolute alcohol cooled to 0°. To this were added 1·08 grams of phenylhydrazine dissolved in 20 c.c. of absolute alcohol and similarly cooled. The liquid containing the perbromide was rapidly stirred during the addition, and cooled in a freezing mixture, the temperature never being allowed to rise above zero. The orange-coloured benzenediazonium perbromide was gradually transformed into the almost colourless diazonium bromide, which, when the whole of the hydrazine had been added, subsided as a very pale yellow, crystalline powder. To separate the whole of the diazonium bromide from the slightly brown mother liquor, 100 c.c. of dry ether were added. The salt was then collected, washed with dry ether, and dried over sulphuric acid in a vacuum, light being excluded. In two experiments carried out as above, 4·9 and 5·1 grams of benzenediazonium bromide were obtained, the theoretical yield being 5·55 grams. The purity of the product was confirmed by an estimation of the bromine:

0·8865 gave 0·8976 AgBr. Br = 43·09.

$C_6H_5N_2Br$ requires Br = 43·20 per cent.

A quantity was also converted into benzeneazo-β-naphthol.

The reaction can be carried out equally advantageously in presence of acetic acid. 6·9 Grams of benzenediazonium perbromide, very finely powdered, were suspended in 12 c.c. of glacial acetic acid and cooled as before. To this was added 1·08 grams of phenylhydrazine, dissolved in 6 c.c. of acetic acid, care being taken to add the latter so slowly that the temperature of the mixture never rose above zero. The perbromide gradually disappeared as before, and a white deposit of the diazonium bromide subsided, which passed into solution on allowing the temperature to rise slightly, a pale reddish-coloured liquid resulting. One hundred c.c. of dry ether were then added, when the benzenediazonium bromide separated as an almost white, crystalline powder, which was collected, washed with ether, and dried in a vacuum over sulphuric acid, light being excluded. The yield reached 97 per cent. of the theoretical. The purity of the product was ascertained as before.

Preparation of o-*Toluenediazonium Bromide.*

This was prepared in a precisely similar manner from *o*-toluenediazonium perbromide and *o*-tolylhydrazine, using, however, a smaller quantity of alcohol or of acetic acid and a larger amount of ether. *o*-Toluenediazonium bromide separated as a yellowish-white, crystalline powder, which dissolved very readily in cold alcohol and crystallised in faintly yellow-coloured, small prisms on the addition of ether. It is a remarkably deliquescent compound, liquefying after a few minutes' exposure to damp air.

Preparation of p-*Toluenediazonium Bromide.*

p-Toluenediazonium perbromide and *p*-tolylhydrazine react similarly, producing *p*-toluenediazonium bromide, which dissolves readily in alcohol and separates in small, faintly yellow-coloured prisms on the addition of ether. It is extremely deliquescent, and soon liquefies if exposed to moist air. The purity of this and of the preceding compound was established as before by estimating the bromine, and by converting them into the corresponding tolueneazo-β-naphthols.

Both the toluenediazonium bromides are so deliquescent that they can only be obtained in a solid state if anhydrous solvents are used. If any water is present, they separate on addition of ether as oily liquids, which can only be made to solidify with difficulty by dissolving in anhydrous alcohol and reprecipitating by perfectly dry ether.

p-Bromobenzenediazonium bromide has been prepared similarly from *p*-bromobenzenediazonium perbromide and *p*-bromophenylhydrazine.

The thanks of the author are due to the Government Grant Committee of the Royal Society for a grant which has partly met the cost of the material, and to Dr. Baker for allowing him the use of the Christ Church Laboratory.

CHRIST CHURCH,
OXFORD.

XCII.—*The Absorption Spectrum of Camphor.*

By WALTER NOEL HARTLEY, D.Sc., F.R.S.

WITH a view to determining the nature of their atomic absorption, various homocyclic compounds were examined and compared with the spectra of benzene and its derivatives, both with regard to the intensity of the general absorption and the presence or absence of an absorption band. The typical substances for comparison were principally the hydroaromatic hydrocarbons, benzene hexachloride, camphor oil, camphoric acid, and camphor (Hartley and Huntington, *Proc. Roy. Soc.*, 1880, **31**, 1; W. N. Hartley, Trans., 1881, **39**, 153.)

It was pointed out that any one of the formulæ proposed for camphor and camphoric acid at that time would be consistent with these substances being compounds with a more diactinic character than either benzene and its homologues or the terpenes. Neither camphor oil nor camphoric acid showed any absorption band, and both substances transmitted the ultraviolet rays more freely than hydroaromatic derivatives. Of the several specimens of camphor examined, only three were described.

No. 1.—Crystals of camphor which had separated from camphor oil boiling between 200° and 220°.

No. 2.—A specimen of the finest commercial camphor, which was resublimed prior to its examination.

No. 3.—Fine crystals of camphor, spontaneously sublimed from a quantity of the solid No. 2, placed in a capacious bell-jar, and exposed for many days to the action of sunlight. As is well known, camphor vapour condenses on the sides of the glass most exposed to the sun's rays. In this instance, the best crystals obtained were 5 mm. in length by 2·5 mm. in width, of perfect transparency, and a brilliant appearance. These were selected for examination. The specimens No. 1

and No. 2 exhibited an absorption band which, on account of its feeble character as compared with bands seen in the spectra of benzene derivatives, and the ease with which dilution caused the disappearance of the band, was thought to be due to some impurity.

No. 3, on the other hand, transmitted a continuous spectrum, "and was, in fact, so transparent that a solution in alcohol containing 1/500th of the substance transmitted all rays less refrangible than Cd 25. This far exceeds in diactinic quality the numerous specimens of terpenes I have examined."

Having made preparations in the summer of 1907 for re-examining this substance, I became aware that Baly, Marsden, and Stewart had been led to the conclusion that camphor shows an absorption band but camphoroxime does not (Trans., 1906, **89**, 979), and that the band is attributed to the "reactivity" of the carbonyl and the neighbouring CH_2 groups. These authors state that their solution was ten times as strong as that examined by me. If this were so, but of that I am doubtful, it might account for the difference between their conclusions and mine with respect to camphor. As the matter is of considerable interest, I have for my own satisfaction continued the experiments which had been projected.

As camphor readily forms solid solutions of substances presented to it in a state of vapour, it was difficult to obtain it quite free from minute traces of such compounds as would affect its absorption spectrum; but the refining of camphor on a manufacturing scale has now been carried to a state of great perfection, and I am indebted to Mr. W. E. B. Blenkinsop, of the firm of May and Baker, Ltd., of Battersea, for an ample supply of the doubly-refined material. This was again submitted to sublimation, but in the absence of sufficient sunlight the warmth of a 10-candle-power electric glow lamp placed in a bell-jar of about 5 litres capacity was substituted. The crystals as deposited were observed with a low power microscope; they were all in stellate groups, with the exception of a single crystal of small size. In this respect, they differed from the large crystals obtained in 1881 by the action of sunlight.

To ascertain whether the crystals were homogeneous, the original sample, the resublimed substance, and, lastly, the residue remaining after about five-sixths had been sublimed were each examined separately.

The concentration was ten times that usually examined, being one centigram-molecule in 100 c.c. of absolute alcohol.

Measurements of the Absorption Band Observed in Specimens of Camphor Solutions at Different Concentrations.

Camphor No. 1.—Doubly refined.

At. wt.	Solution.	Thickness of layer of solution in mm.				
152	*N*/10	49	25	15	10	5
	1·52 grams in 100 c.c. of alcohol	1/λ Rays transmitted to	1/λ	1/λ Band	1/λ Band	1/λ Band Very feeble
		3064	3190	**3190** to **3886**	**3210** to **3720**	**3455** to **3692**

At 4 mm. there is a complete transmission of all rays to 1/λ 3954, and at 0·5 mm. all rays are transmitted to 1/λ 4673.

Camphor No. 2.—Sample No. 1, resublimed.

This differs but very slightly from No. 1, in the continuous rays being transmitted feebly between 1/λ 3455 and 1/λ 3692 in a thickness of 5 mm., whereas in No. 1 there is a band at this point.

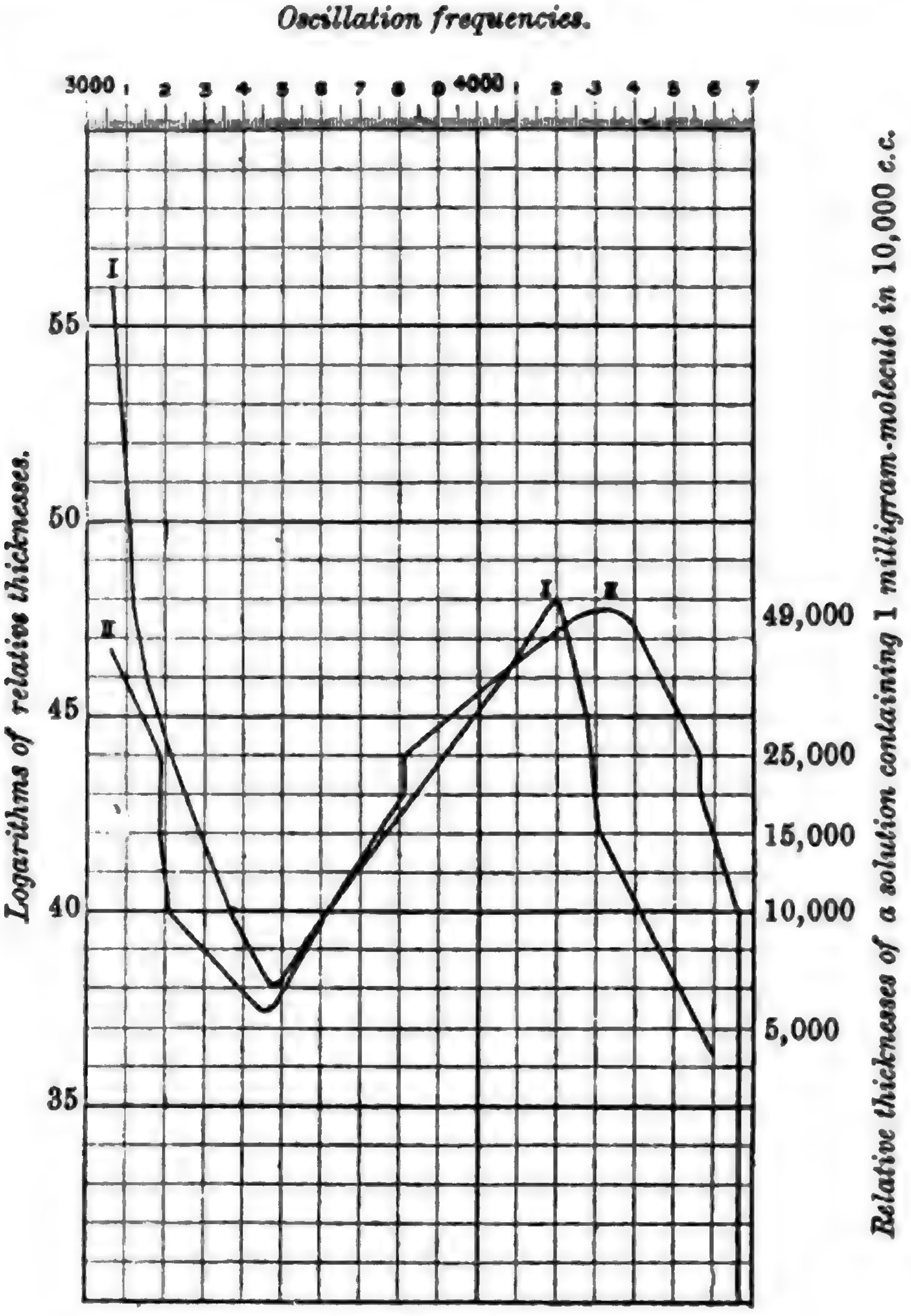
Camphor No. 3.—Residue from No. 2, after sublimation.

The photographs differed slightly from the foregoing, the absorption band being somewhat stronger even than in No. 1.

To determine more accurately the termination of the band and the extent of the transmitted spectrum beyond this point, the instrument was carefully focussed for the more refrangible rays.

Concentration, 1 *Centigram-molecule in* 100 *c.c.*

Layer of liquid examined.	Proportional thicknesses of solution containing 1 milligram-molecule in 10,000 c.c.	Termination of band. 1/λ	Rays transmitted to 1/λ
49 mm.	49,000 mm.	4176	4411
39 ,,	39,000 ,,	4037	4460
30 ,,	30,000 ,,	3817	4552
20 ,,	20,000 ,,	3817	4552
10 ,,	10,000 ,,	3635	4662
5 ,,	5,000 ,,		4671



Camphor.

Curve I. According to Baly, Marsden, and Stewart.
Curve II. Hartley.—Sample doubly refined.

Concentration, 1 *Centigram-molecule in* 100 *c.c.*

The less refrangible rays were accurately focussed so as to give the position of the less refrangible edge of the band:

Layer of liquid examined.	Proportional thicknesses of solution containing 1 milligram-molecule in 10,000 c.c.	Commencement of band. $^1/\lambda$
49 mm.	49,000 mm.	3064
25 ,,	25,000 ,,	3190
15 ,,	15,000 ,,	3190
10 ,,	10,000 ,,	3210
5 ,,	5,000 ,,	Indication of a band at 3500. $^1/\lambda$

Concentration 1 *Milligram-molecule in* 100 *c.c.*

Focussed for the more refrangible rays:

Layer of liquid examined.	Proportional thicknesses of solution containing 1 milligram-molecule in 10,000 c.c.	Termination of spectrum. $1/\lambda$
10 mm.	10,000 mm.	4673
5 ,,	5,000 ,,	4673
3 ,,	3,000 ,,	4673

The absorption band and the curve drawn is not precisely identical with that observed by Baly, Marsden, and Stewart, and their curve has been introduced for comparison.

The specimens of camphor more recently examined transmit the rays lying beyond the band more freely.

Conclusion.

The band observed in the spectrum belongs to camphor, and it is accounted for by the juxtaposition of the CO and CH_2 groups in the molecule.

The absorption band being a shallow one, and observed only in more concentrated solutions than those of benzene, would account for its not being photographed in solutions containing 1/500th of camphor. The various specimens of camphor originally examined, with the exception of that described as No. 3, undoubtedly did contain an impurity which was not improbably cymene.

I desire to express my thanks to Mr. A. G. G. Leonard, A.R.C.Sc.I., for the care he has exercised in taking the latter photographs and drawing the curves, and to Mr. W. E. B. Blenkinsop for the camphor presented to me.

Royal College of Science, Dublin.

XCIII.—*The Chemical Action of Radium Emanation. Part III. On Water and Certain Gases.*

By Alexander Thomas Cameron and Sir William Ramsay, K.C.B.

The first paper of this series (Trans., 1907, **91**, 931) contained (p. 941) a table of measurements of the rate of decomposition of water by radium emanation. The curve obtained by plotting the rate of increase of the gas volume against time was not exponential; in character it resembled the curve representing the decay of the emanation, but its period of half value was 2·53 days, that of the emanation being 3·86 days. The method of experiment caused a constant change in the ratio of the volumes of the gas and water phases; this probably explains the discrepancy observed. It appeared desirable to make further experiments in this direction.

An apparatus was devised in which both gas and water phases were kept constant, the changes in the amount of gas being read by the pressure it exerted. Under such conditions the emanation, if it obeys Henry's law, should divide itself in a definite ratio between the two phases, and, since it appears certain that the medium containing it does not affect its rate of decay (see Moore, *Proc. Roy. Soc.*, 1908, **80**, *A*, June), the ratio of emanation in the water phase to emanation in the gas phase should remain constant throughout the whole experiment.

The results obtained were simple. The curve showing rate of decomposition was exponential; the period representing the total action approximated more closely to that of the half decay of the emanation (3·86 days) the more exact the experimental data.

Similar results were obtained for the recombination of hydrogen and oxygen, and these were so successful that it appeared desirable to extend the observations to other gases. Great stress cannot be laid on the quantitative results in these experiments; they must be regarded as preliminary investigations. The qualitative results, however, seem to be of sufficient interest to merit immediate publication.

It was found that carbon dioxide is decomposed into carbon, oxygen, and carbon monoxide; carbon monoxide into carbon, oxygen, and carbon dioxide; ammonia is converted in considerable quantity into nitrogen and hydrogen; the component gases recombine in less amount for the same quantity of emanation present. Hydrogen chloride is decomposed into hydrogen and chlorine, and the absorption of the latter by mercury permits measurement of the rate of action. So far the only gas tested in which the action of the emanation was not discernible is steam, this being particularly remarkable in view of the comparatively rapid decomposition of water in the same circumstances. In all, twenty experiments have to be recorded, four with water, five with hydrogen and oxygen, three with carbon dioxide, the same number with ammonia, and single experiments with carbon monoxide, hydrogen chloride, nitrogen and hydrogen, electrolytic gas at 130°, and steam at 130°.

Apparatus and Method of Experiment.

The apparatus used for most of the experiments was a modification of that described in a previous paper (Trans., 1907, **91**, 1267), and employed to measure the emanation itself. It is shown in Fig. 1. The method varied considerably with the experiment. In general, the gas to be tested was taken through the inverted siphon, *A*, into the burette, *C*, and then, by reversing the stopcock, *B*, allowed to enter the rest of the apparatus (previously pumped empty through *F*). By closing the stopcock, *H*, and allowing the mercury to rise through *J*, the amount of gas in the apparatus could be gauged, and more added, or part removed through the pump, as found desirable. Finally, the apparatus between the stopcock, *H*, and the taking-in burette was again exhausted through *F*. The electrolytic gases containing emanation, which had accumulated over a solution of radium salt during several days, were introduced through the inverted siphon, and exploded in the burette, *C*. If hydrogen was one of the products of decomposition of the tested gases (for example, with ammonia or hydrogen chloride), the residual excess of hydrogen, containing the emanation, was forced through the apparatus by raising the mercury, caused to pass through the phosphoric oxide tube, and finally added to the gases to be experimented with through the tap, *H*. *H* was then closed, and the mercury level raised to the point *N*, the pressure being given by the barometric

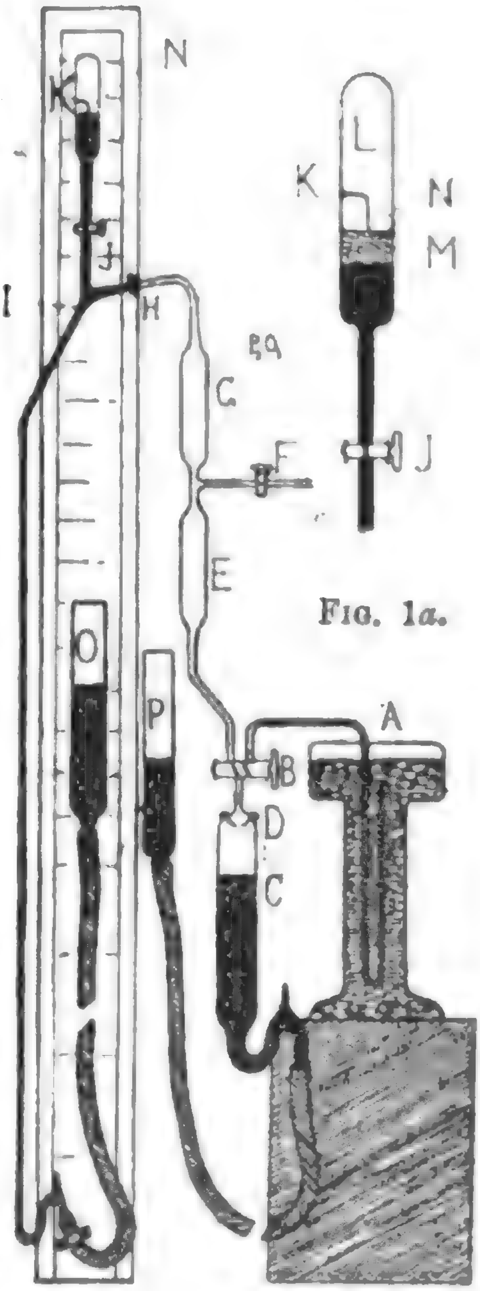


Fig. 1a.

Fig. 1.

pressure less the difference of level between *N* and the mercury in the reservoir, *O*. The tap *J* was closed. Readings were taken daily, and usually extended over a period of three or four weeks.

Where not hydrogen, but oxygen, was a product of the reaction, the excess of hydrogen was exploded with about its own volume of oxygen, and the remaining oxygen and emanation added in the same way.

Where the method differed largely from that described, an account will be given under the heading of the particular experiment. That employed for the first experiment was essentially different, and may be described here. No phosphoric oxide tube was used in this case or in any similar case when water or a gas absorbable by the pentoxide was employed. The electrolytic gases containing the emanation were exploded, and a small quantity of water taken over into the burette along with the excess of hydrogen. The water and hydrogen were then introduced into the bulb *E* (by raising the mercury reservoir *P*), and water and emanation frozen by jacketing with liquid air. The excess of hydrogen was pumped off through *F*, and then water and emanation forced over through *H* and *J* into the measuring bulb (Fig. 1*a*). The point *N* was set against the lower surface of the water, and the stopcock *J* closed. In this way the gas phase, *L*, and the water phase, *M*, were definitely fixed. Daily readings were taken; the point was always set to the under surface of the water, and the pressure read. The two phases thus had always definite constant volumes, since the amount of water decomposed was never great enough to affect its volume appreciably.

Since these experiments occupied a considerable time, it was convenient to perform several simultaneously. For this purpose the measuring bulb *K* was replaced by an apparatus of the kind shown in Fig. 2. The bulbs were separately filled with different gases or water, and the taps turned. The emanation with hydrogen or oxygen, as found desirable, was allowed to rise to the level *K*, when it divided itself according to the volumes of the tubes between the taps and the horizontal bend, and each part in turn could be allowed to enter its special bulb. By calibration of the tubes afterwards, it was found possible to calculate what percentage of the total quantity of emanation was employed in any particular experiment.

In the figure, the bulb *A* was used for hydrogen chloride. Since the formation of mercury chloride seemed likely to render readings against a point difficult, a scale, *E*, was fixed to the tube, and the mercury level altered from time to time. A cup-shaped bulb was employed, the depression, *F*, containing mercury; the downward flow of mercury vapour thereby produced caused much more rapid absorption of any chlorine liberated.

Tube *B* contained a point, and was packed with phosphoric oxide enclosed between plugs of glass wool. It was used for dry hydrogen and oxygen in order to measure the total recombination produced, the water being absorbed as fast as formed.

Tube *C* only contained a point, and was of the type used for ammonia, carbon dioxide, and carbon monoxide.

Tube *D* was the type employed for the final experiments with water. The water was introduced through the side-tube *H* from a weighed wash-bottle; the amount of water was ascertained by difference. The side-tube was then sealed with the blow-pipe. In this way much more exact measurements were obtained.

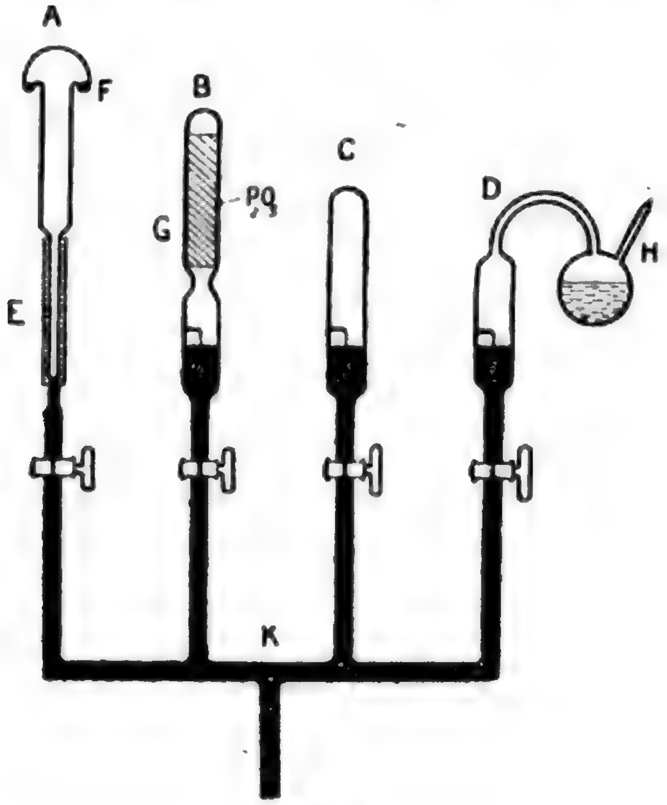


FIG. 2.

In order to convert the pressure readings into exact volume measurements, it was necessary to calibrate the space enclosed by the mercury surface set at the point. Where possible this was done by filling the space with mercury, which was then weighed.

For the later experiments with ammonia and with nitrogen and hydrogen, an entirely different apparatus was devised. This in some ways leads to more correct results, and it obviates the necessity of a pump.

By raising the reservoir, *K*, and lowering *G* (Fig. 3), and drawing gas from *E*, and by turning the stopcock *B* and then forcing the gas through *A*, the apparatus itself serves as a pump, and in this way it can be completely filled with mercury. The actual burette used contained points as at *D*, the volumes to these points being accurately known. The method of using this measuring apparatus has been described by one of us previously (*Proc. Roy. Soc.*, 1905, **76**, *A*, 113; Trans., 1907, **91**, 939).

The gas to be tested is taken into the burette through the inverted siphon, and accurately measured; emanation and excess of hydrogen are added, and the total volume again measured. By reversing the tap *B*, raising the reservoir *G*, and lowering *K*, the gas can be forced into *E*, and the pressure read as usual. The tap *F* is closed except when readings are being taken. Since the original volume has been determined, the space *E* to the point *H* is thereby immediately calibrated.

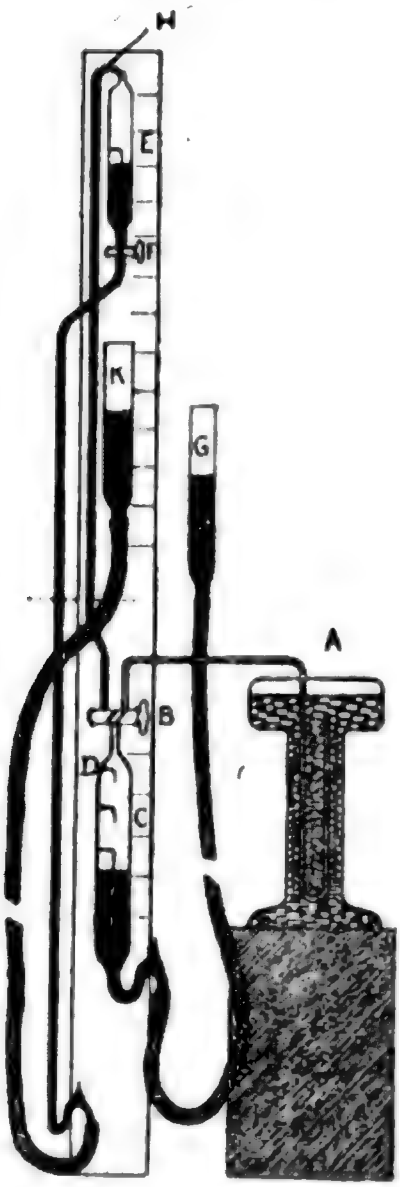


FIG. 3.

Errors in some of the earlier experiments are considerable, as the methods employed, especially in calculating, were only gradually perfected, particularly as regards the measurement of the water space. Whenever readings were taken with the original apparatus, bubbles passed up through the taps. These appeared to be due, not to external leakage, but to the action of a trace of emanation trapped at the taps, on the tap-grease; the gas was probably carbon dioxide. As the emanation decayed, the size of the bubble diminished. Finally, no bubble was formed; moreover, in the experiments with the apparatus in Fig. 3, where emanation did not come into contact with the tap *F*, no such phenomenon occurred. As far as possible, the pressures were measured before and after a bubble passed up, and the error thus eliminated.

The part of the apparatus in Fig. 3 below the dotted line could also be used very simply to calibrate tubes, such as *B* and *D* (Fig. 2), the nature of which would not permit them to be filled with mercury. These were cut off below the taps, and rubbered on to the capillary tube cut at *L*. Mercury was forced up into *B*, say, and set at the point, the pressure being read as usual. Part of the gas was then drawn into *C*, the tap *B* turned, and the gas below measured, then rejected through *A*. Finally, the mercury was again set at the point in *B*, and the pressure again read. The difference of pressure ($P_0 - P$) was that exerted by the amount of gas measured (V, say), so that the volume of B to the mercury-point surface is given by $\frac{V.760}{P_0 - P}$.

In the detailed account of the experiments which follows, it has been found convenient to give the amount of the emanation used in terms of the amount produced from one gram of radium (metal) in 3·86 days.* *This quantity is called E.* In all cases the pressure readings have been corrected for expansion of mercury and gas to 0°, and, where necessary, for the vapour pressure of water.

Experiments with Water and with Hydrogen and Oxygen.

Experiment 1.—The method employed has been indicated (p. 968). The tube was calibrated by mercury, and, since the water space was not large, the error in this calibration is certainly not negligible. The result gave gas space 1·267 c.c., water space 0·291 c.c. The amount of emanation used was that collected during six days from a solution containing 101 milligrams of radium bromide and 10 milligrams of radium sulphate. This is equivalent to 0·0806 E. In the fourth and fifth columns, V_∞ is the final volume, V_o the initial volume, and V_t the volume at time t.

Time in days.	Pressure in mm.	Volume in c.c.	$V_\infty - V_t$.	$100\frac{V_\infty - V_t}{V_\infty - V_o}$.	$\log\left\{100\frac{V_\infty - V_t}{V_\infty - V_o}\right\}$.
0	9·0	0·015	0·766	100	2·000
1·06	69·4	0·116	0·665	86·8	1·938
1·98	90·0	0·150	0·631	82·4	1·916
3·04	166·2	0·277	0·504	65·8	1·818
4·08	226·1	0·377	0·404	52·7	1·722
5·08	269·7	0·450	0·331	43·2	1·635
6·04	305·5	0·509	0·272	35·5	1·550
7·21	345·4	0·576	0·205	26·8	1·428
7·92	360·0	0·600	0·181	23·6	1·373
9·00	377·3	0·629	0·152	19·8	1·297
10·04	395·9	0·659	0·122	15·9	1·201
11·05	409·4	0·682	0·099	12·9	1·111
12·10	418·0	0·697	0·084	11·0	1·041
12·98	428·3	0·714	0·067	8·7	0·939
14·09	436·4	0·728	0·053	6·9	0·839
15·05	438·0	0·730	0·051	6·7	0·826
17·09	450·0	0·750	0·031	4·0	0·602
18·12	455·3	0·759	0·022	2·9	0·462
19·01	458·6	0·765	0·016	2·1	0·322
20·08	460·4	0·768	0·013	1·7	0·230
21·02	459·5	0·766	0·015	2·0	0·301
21·91	457·7	0·763	0·018	2·3	0·362
105·0	468·5	0·781	0·000	0·0	

---

* In experiments 1, 2, 5, 6, and 7, the emanation was obtained from 101 milligrams of radium bromide and 10 milligrams of radium sulphate; in the remaining experiments, from a mixture of radium bromide and carbonate, corresponding with 431 milligrams of bromide. The calculations are based on the assumptions that the formulæ $RaBr_2,2H_2O$ and $RaSO_4$ are correct, that the atomic weight of radium is 226·5, and that the period of half decay of the emanation is 3·86 days.

The curve obtained by plotting the figures in the fifth column against the time, and the logarithmic curve (sixth column against time) are shown in Fig. 4. Their significance will be considered later.

Experiment 2.—The experiment was one of three conducted simultaneously. Water was introduced into the measuring bulb

Decomposition of water.

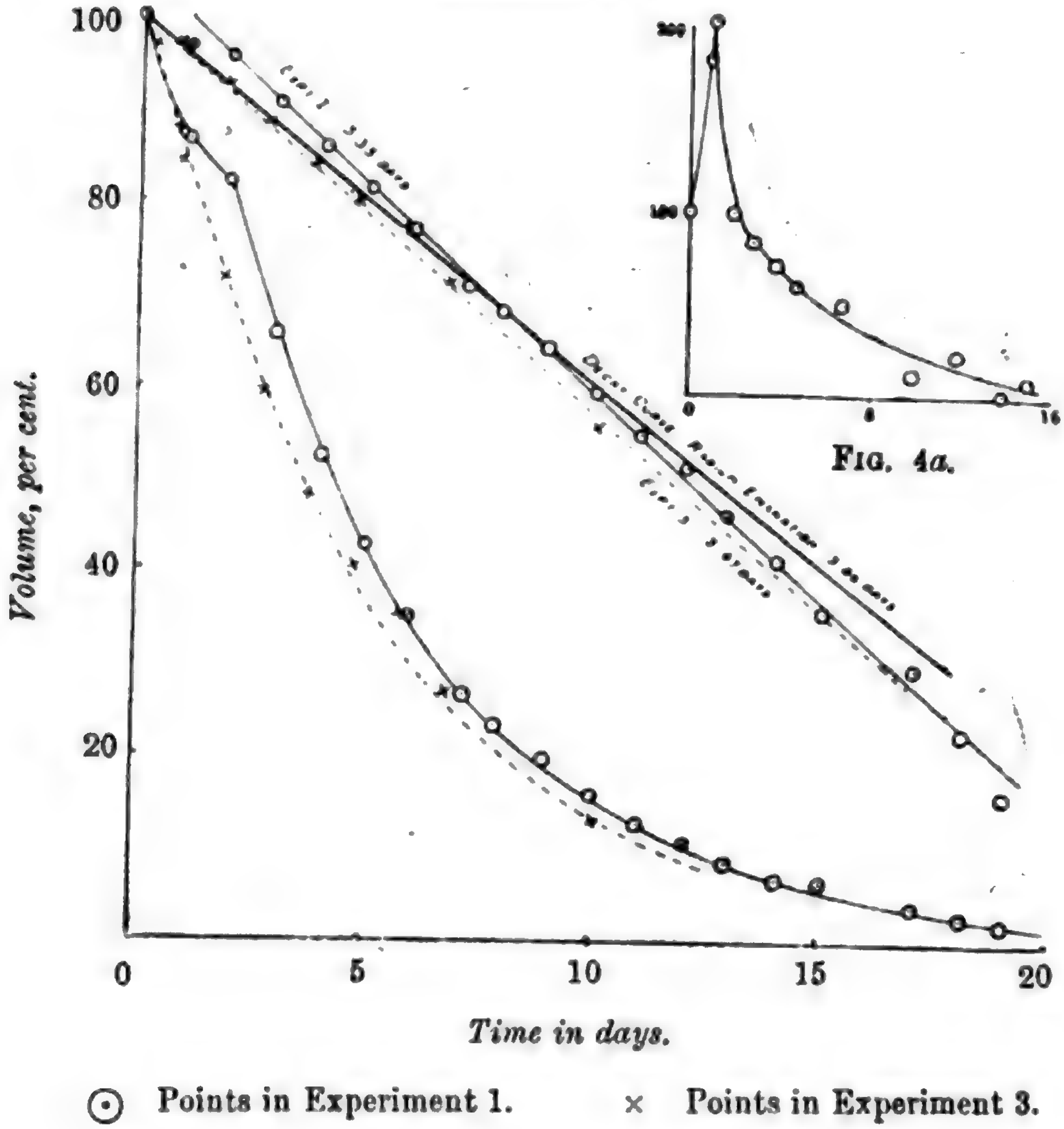


FIG. 4.

before sealing it to the apparatus, and the height of water read and afterwards calibrated with mercury; the error in this case is possibly large. The mixed electrolytic gases containing emanation were admitted after exploding a portion of them, there being therefore a slight excess of hydrogen. The emanation used was equivalent to 0·050 E. The gas space was 3·297 c.c., the water space 0·427 c.c.

Time in days.	Pressure in mm.	Volume in c.c.	$V_\infty - V_t$.	$100\frac{V_\infty - V_t}{V_\infty - V_t}$.
0	632·2	2·742	0·110	100·0
0·89	653·2	2·833	0·201	182·7
1·07	658·9	2·858	0·226	205·4
1·96	632·0	2·741	0·109	99·1
2·84	627·9	2·724	0·092	83·6
3·80	624·9	2·710	0·078	70·9
4·80	622·0	2·698	0·066	60·0
6·80	619·4	2·687	0·055	50·0
9·88	609·4	2·643	0·011	10·0
11·91	612·4	2·657	0·025	22·7
13·80	607·1	2·633	0·001	0·9
15·00	609·1	2·642	0·009	8·2
15·79	604·1	2·620		
16·85	607·6	2·638	0·006	5·6
21·89	606·7	2·632	0·000	0·0

The results are irregular, and the whole volume-change small. The curve obtained by plotting the figures in column 5 against time is shown in Fig. 4*a*.

The gases were analysed at the conclusion of the experiment, with the following result:

Hydrogen	1·815	c.c.
Oxygen	0·634	,,
Nitrogen and carbon dioxide.........	0·016	,,
Total volume	2·465	,,

A trace of gas not pumped off would account for the difference in volume.

Experiment 3.—The experiment was one of three conducted simultaneously. Water was pipetted into the bulb, as described previously, from a minute wash-bottle, and the amount ascertained by weighing the bottle before and after. The whole bulb was calibrated afterwards, the gas and water volumes being exactly known. (Gas space, 3·789 c.c.; water space, 2·302 c.c.) The emanation was introduced with excess of oxygen, and was equivalent to 0·062 E. At the end of ten days, considerable leakage unfortunately occurred. The real final value was accordingly determined by extrapolation.

Time in days.	Pressure in mm.	Volume in c.c.	$V_\infty - V_t$.	$100\frac{V_\infty - V_t}{V_\infty - V_0}$.	$\log 100\frac{V_\infty - V_t}{V_\infty - V_0}$.
0	39·9	0·200	0·390	100	2·000
0·25	42·5	0·212	0·378	96·9	1·986
0·81	49·7	0·248	0·342	87·7	1·943
0·92	52·6	0·262	0·328	84·1	1·925
1·89	62·8	0·310	0·280	71·8	1·856
2·80	71·8	0·358	0·232	59·5	1·774
3·81	80·5	0·401	0·189	48·5	1·685
4·81	86·4	0·431	0·159	40·8	1·610
5·81	90·4	0·451	0·139	35·6	1·552
6·81	97·0	0·484	0·106	27·2	1·434
10·07	107·9	0·538	0·052	13·3	1·125
∞		(0·590)	—	0·0	

The gas was analysed, and found to contain 0·272 c.c. of oxygen (after deducting the amount due to air leakage), and 0·343 c.c. of hydrogen, giving a total volume of 0·615 c.c., which agrees fairly closely with the extrapolated value.

The curves are shown in Fig. 4.

A further experiment was carried out in the same way. At the end of six days, a vacuum was created below the tap (Fig. 2, *D*), and a clear passage to the pump was left; the tap was turned for about two seconds. The gas below the tap was then pumped off, and readings continued for eleven days more. The change of volume in the second part of the experiment was much slower (0·058 c.c. in the eleven days, as compared with 0·728 c.c. in the first six days), proving that the emanation makes its escape from the water phase to a vacuum above almost instantaneously. The first curve was not exponential, but there were an insufficient number of points to determine its nature accurately.

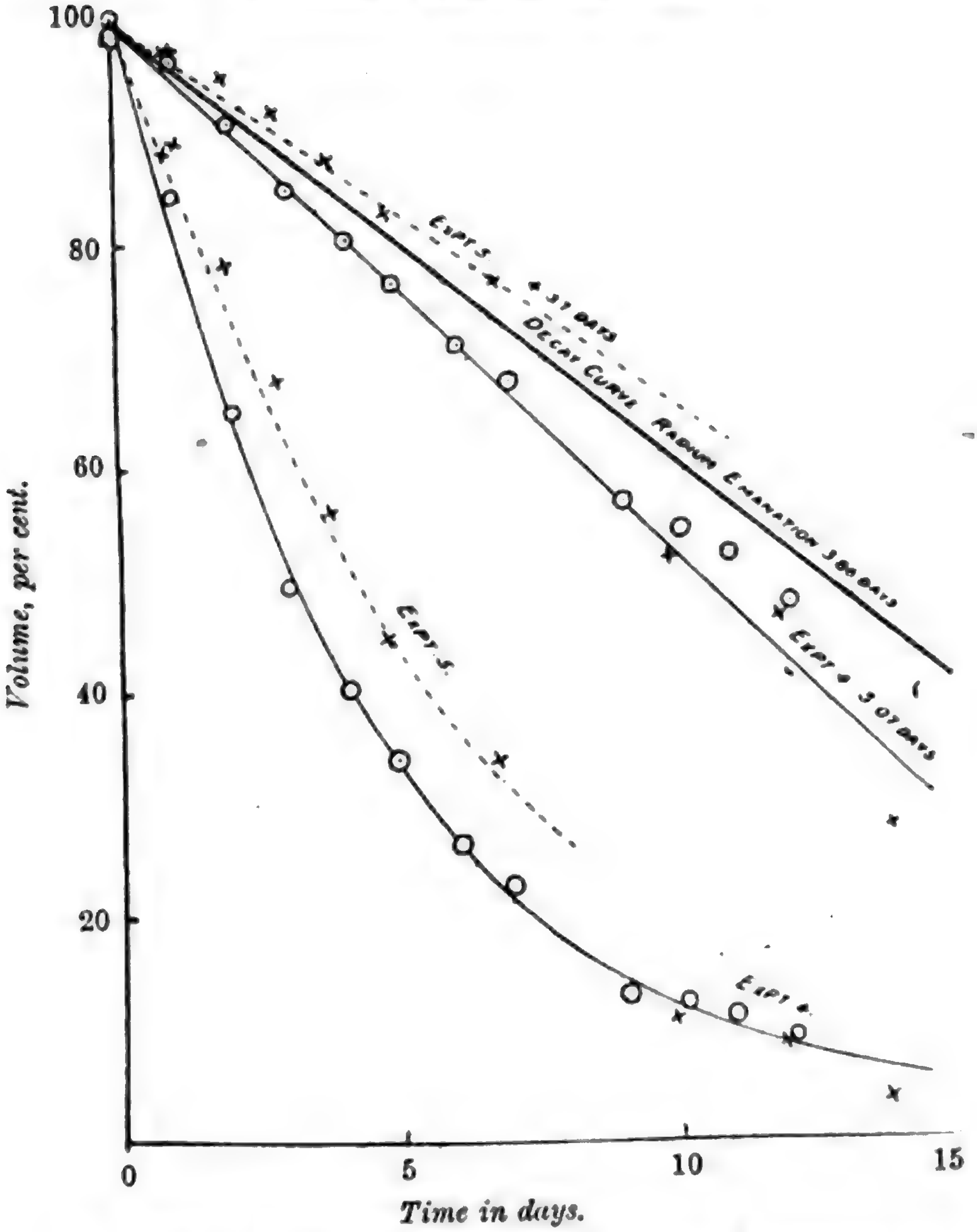
Experiment 4 (*Moist Hydrogen and Oxygen*).—The electrolytic gases, with emanation, were exploded down to reasonable bulk, and introduced into the measuring bulb. They contained therefore excess of moisture throughout the experiment. The emanation corresponded with 0·093 E. The volume of the measuring tube was 2·186 c.c.

Time in days.	Pressure in mm.	Volume in c.c.	$V_t - V_\infty$.	$Q = 100\frac{V_t - V_\infty}{V_0 - V_\infty}$.	log Q.
0	523·5	1·505	0·668	100	2·000
0·03	519·8	1·495	0·658	98·5	1·993
1·02	487·0	1·401	0·564	84·4	1·926
2·07	442·0	1·271	0·434	65·0	1·813
3·07	405·6	1·167	0·330	49·4	1·694
4·13	384·5	1·106	0·269	40·3	1·605
4·99	369·5	1·063	0·226	33·8	1·529
6·11	352·2	1·013	0·176	26·3	1·420
7·07	343·5	0·988	0·151	22·6	1·354
9·11	321·4	0·924	0·087	13·0	1·114
10·16	319·3	0·919	0·082	12·3	1·090
11·04	316·6	0·911	0·074	11·1	1·045
12·10	312·3	0·898	0·061	9·1	0·959
97·0	291·0	0·837	0·000	0·0	

The curves are shown in Fig. 5.

Experiment 5 (*Moist Hydrogen and Oxygen*).—This, exactly similar to the previous experiment, was one of three conducted simultaneously. The amount of emanation was equivalent to 0·025 E. The volume of the measuring tube was 2·79 c.c.

Combination of hydrogen and oxygen.



⊙ Points in Experiment 4. × Points in Experiment 5.

FIG. 5.

Time in days.	Pressure in mm.	Volume in c.c.	$V_t - V_\infty$.	$Q = 100\frac{V_t - V_\infty}{V_0 - V_\infty}$.	log Q.
0	564·5	2·073	0·221	100	2·000
0·89	557·4	2·047	0·195	88·2	1·945
1·07	558·0	2·049	0·197	89·1	1·950
1·96	551·4	2·025	0·173	78·3	1·894
2·84	545·0	2·002	0·150	67·9	1·832
3·80	538·0	1·976	0·124	56·1	1·749
4·80	531·2	1·951	0·099	44·8	1·651
6·80	524·7	1·927	0·075	33·9	1·530
9·88	510·8	1·876	0·024	10·9	1·037
11·91	509·3	1·871	0·019	8·6	0·934
13·80	506·5	1·860	0·008	3·6	0·556
15·00	502·1	1·844	—	—	
15·79	504·0	1·851	—	—	
16·85	505·6	1·857	0·005	2·7	0·431
21·89	504·3	1·852	0·000	0·0	

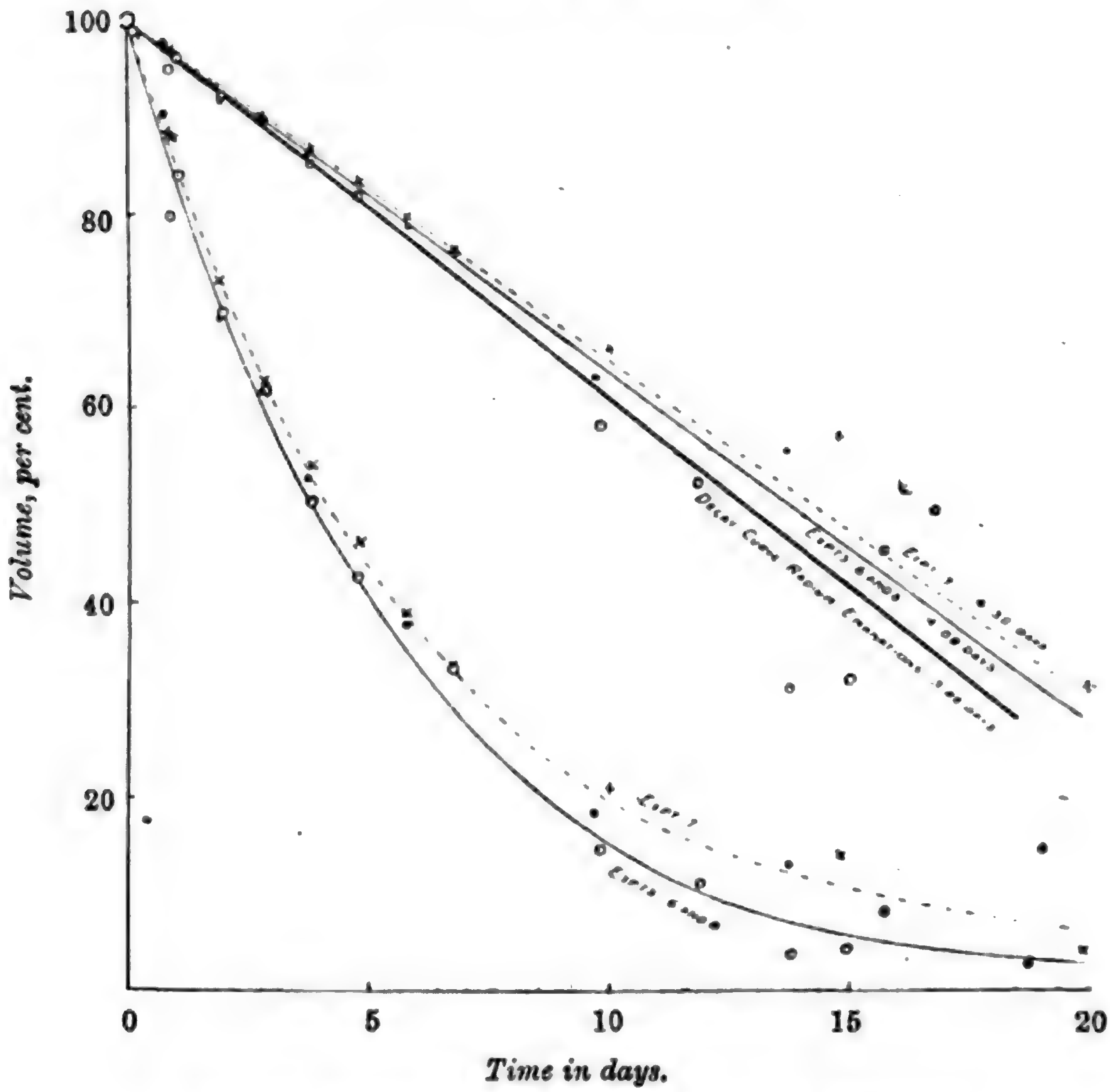
The curves are shown in Fig. 5. The gases were analysed, with the result:

Hydrogen	1·253 c.c.
Oxygen	0·579 ,,
Nitrogen and carbon dioxide	0·008 ,,
Total volume	1·840 ,,

The measured and final volume thus agree very closely.

Experiment 6 (*Dry Hydrogen and Oxygen*).—The method was that usually employed, the measuring tube containing phosphoric oxide (as in *B*, Fig. 2). The amount of emanation used was equivalent to 0·044 E. The volume of the tube was 4·996 c.c.

Combination of hydrogen and oxygen.



⊙ Points in Experiment 6. × Points in Experiment 7.

● Points in Experiment 8.

FIG. 6.

Time in days.	Pressure in mm.	Volume in c.c.	$V_t - V_\infty$.	$Q = 100\frac{(V_t - V_\infty)}{V_0 - V_\infty}$.	log Q.
0	577·6	3·798	0·555	100	2·000
0·89	560·6	3·686	0·443	79·8	1·802
1·07	564·1	3·709	0·466	84·0	1·924
1·96	552·4	3·631	0·388	69·9	1·844
2·84	546·9	3·595	0·352	63·4	1·802
3·80	535·6	3·522	0·279	50·3	1·702
4·80	530·2	3·485	0·242	43·6	1·639
6·80	521·5	3·428	0·185	33·3	1·522
9·88	505·6	3·324	0·081	14·6	1·164
11·91	502·8	3·305	0·062	11·2	1·049
13·90	496·4	3·264	0·021	3·8	0·580
15·00	496·9	3·267	0·024	4·3	0·633
15·79	500·2	3·288	0·045	8·1	0·908
16·85	501·7	3·297	0·054	9·7	0·987
21·89	493·3	3·243	0·000	0·0	

The curves are shown in Fig. 6. Analysis of the gas gave the result:

Hydrogen	2·267	c.c.
Oxygen	1·004	,,
Nitrogen and carbon dioxide	0·019	,,
Total volume	3·290	,,

Here, also, there is a close agreement between the measured and the calculated volumes.

Experiment 7 (*Dry Hydrogen and Oxygen*).—The experiment was one of three conducted simultaneously. The tube was filled with electrolytic gas, and oxygen, containing emanation equivalent to 0·103 E, was added. The volume of the tube was 3·432 c.c. at N.T.P.

Time in days.	Pressure in mm.	Volume in c.c.	$V_t - V_\infty$.	$Q = 100\frac{V_t - V_\infty}{V_0 - V_\infty}$.	log Q.
0	344·2	1·551	0·526	100	2·000
0·02	343·8	1·549	0·524	99·6	
0·04	344·3	1·552	0·527	100·2	
0·06	344·8	1·557	0·532	101·1	
0·07	344·8	1·557	0·532	101·1	
0·09	343·5	1·551	0·526	100·0	
0·11	343·9	1·553	0·528	100·4	
0·21	342·0	1·545	0·520	98·8	
0·25	341·8	1·544	0·519	98·7	
0·29	340·5	1·538	0·513	97·5	
0·81	330·4	1·490	0·465	88·4	1·946
0·92	329·8	1·488	0·463	88·0	1·944
1·89	312·1	1·410	0·385	73·2	1·864
2·80	299·9	1·356	0·331	62·9	1·799
3·81	289·7	1·310	0·285	54·2	1·734
4·81	280·4	1·268	0·243	46·2	1·665
5·81	271·9	1·230	0·205	39·0	1·591
6·81	266·7	1·202	0·177	33·7	1·528
10·07	251·9	1·138	0·113	21·0	1·322
14·84	242·8	1·098	0·073	13·9	1·143
19·88	231·7	1·047	0·022	4·2	0·623
23·84	227·9	1·031	0·006	1·1	0·041
26·80	226·8	1·025	0·000	0·0	

The bubbles passed up through the tap, and measured (by difference in pressure) throughout the experiment were in all 0·026 c.c. (actual final volume, 1·051). The gas was pumped off and analysed:

Hydrogen	0·586	c.c.
Oxygen	0·415	,,
Carbon dioxide	0·023	,,
Total volume	1·024	,,

The curves are shown in Fig. 6.

Experiment 8 (*Dry Hydrogen and Oxygen*).—This was carried out in exactly the same way as experiment 7. The tube was filled with electrolytic gas of more than 99 per cent. purity. The emanation, equivalent to 0·063 E, was added with excess of hydrogen. The volume of the tube was 1·566 c.c.

Time in days.	Pressure in mm.	Volume in c.c.	$V_t - V_\infty$.	$Q = 100\dfrac{V_t - V_\infty}{V_0 - V_\infty}$.	log Q.
0	469·2	0·967	0·476	100	2·000
0·017	469·1	0·967	0·476	100	
0·73	446·8	0·921	0·430	90·3	1·956
1·93	397·8	0·820	0·329	69·1	1·839
2·73	382·8	0·789	0·298	62·6	1·797
3·75	360·2	0·743	0·252	52·9	1·723
5·80	325·4	0·671	0·180	37·8	1·577
9·77	280·7	0·579	0·088	18·5	1·267
13·78	268·0	0·553	0·062	13·0	1·114
18·76	244·1	0·503	0·012	2·5	0·398
23·86	241·4	0·494	0·003	0·6	$\bar{1}$·778
25·76	239·6	0·491	0·000	0·0	

The gases were not analysed. The curves are shown in Fig. 6.

It is now necessary to consider the significance of the results shown by the curves in Figs. 4 to 6. The emanation decays according to the equation:

$$\frac{v_t}{v_0} = e^{-\lambda t},$$

and falls to half value, according to Sackur's determination, in 3·86 days. In experiments 4 to 8 the volume of gas has decreased continuously, hydrogen and oxygen uniting to form water. The value $(V_0 - V_\infty)$ represents the whole effect of the emanation, the total quantity of gas combined. It corresponds with v_0, the total quantity of emanation acting. At any time t, the amount recombined is given by $(V_0 - V_t)$. It corresponds with $(v_0 - v_t)$, the amount of emanation which has decayed up to time t. The quantity $(V_t - V_\infty)$, is the amount of recombination still to take place, to be brought about by the emanation still undecayed, v_t. If the emanation produced an effect proportional to the amount present, then

$$\frac{V_t - V_\infty}{V_0 - V_\infty} = \frac{v_t}{v_0},$$

from which it follows that

$$\frac{V_t - V_\infty}{V_o - V_\infty} = e^{-\lambda t}, \quad (1)$$

where λ should have the same value, and consequently the time of half action (constant $\div \lambda$) should be 3·86 days.

Exactly the same reasoning applies to the figures in experiments 1—3. In these, the amount of gas is continually increasing; $V_\infty - V_o$ represents the total change equivalent to v_o; $(V_\infty - V_t)$ represents the change yet to be produced after time t, corresponding with the emanation yet undecayed, v_t; wherefore, similarly to (1),

$$\frac{V_\infty - V_t}{V_\infty - V_o} = e^{-\lambda t}. \quad (2)$$

The values in the fifth columns have all been obtained by taking the total change of volume $(V_o - V_\infty)$ as 100, the sixth column containing the corresponding logarithms. The fact that the points on the logarithmic curves in Figs. 4 to 6 lie fairly closely on straight lines, shows that the equations (1) and (2) actually hold for some constant λ.

The following table shows that the time of half action, T, approximates to 3·86 days. It has been determined graphically from the curves. P_o is the initial pressure, and P_∞ the final pressure; their difference gives some criterion of the relative accuracy of each experiment. V_E is the volume of gas which would be decomposed or recombined by E c.c. of emanation (p. 971).

No. of experiment.	$(P_o - P_\infty)$. mm.	$(V_o - V_\infty)$. c.c.	T. days.	λ.	Gas phase. c.c.	Water phase. c.c.	Amount of emanation.	V_E c.c.
1	459·5	0·766	3·35	0·207	1·27	0·29	0·081E	9·46
2	—	0·110 ?	—	—	3·30	0·43	0·050E	(2·20)
3	84·7	0·390	3·47	—	3·79	2·30	0·062E	6·29
4	232·5	0·668	3·40	0·204	2·19	small	0·093E	7·18
5	60·2	0·221	4·37	0·159	2·79	small	0·025E	8·84
6	84·3	0·555	4·08	0·170	5·0	—	0·044E	12·61
7	117·4	0·526	4·30	0·161	3·43	—	0·103E	5·01
8	229·6	0·476	4·08	0·071	1·57	—	0·063E	7·56
		Mean	3·86					
		Theor.	3·86	0·1795				

The fact that the mean value for T exactly coincides with the theoretical value, of course, has no real significance, since the graphic determination is certainly not correct to the second decimal figure. It will be observed that experiments 2, 3, 6, and 7, where the points do not lie well on the curve, represent small changes of pressure and large experimental errors. The converse is true for the other experiments. Since the experiments give exponential curves, the constants of which approximate to those for the emanation, it would appear that in any experiment the chemical action produced by the emanation is strictly proportional to the amount present, and, further, *that every molecule of emanation disintegrating produces a definite chemical effect.* But in experiments 6 to 8, which should be comparable, the gas in each case being dry hydrogen and oxygen, and the condition of experiment the same, the total recombination effected varies within wide limits (calculated for E between 5·01 and 12·62 c.c.). This points to some other factor than the emanation playing a part in the chemical action. Excess of one of the constituents may produce an effect. Pressure appears to be without effect. The curves remain exponential during large changes of pressure. It seems more probable that the surface is the unknown factor. It varies from experiment to experiment, but remains constant during any one experiment. The rate of change is consequently not affected, but the total change is altered. Since in these experiments the surface is large, due to the presence of phosphoric oxide, they are unsuitable for the determination of the part played by it in the reaction. In experiments 4 and 5, where the gases were moist and the surface was small, since plain measuring tubes were employed, the agreement is much closer.

We have assumed that the emanation obeys Henry's law, and divides itself in a constant ratio between the gas and water phases, as in the first three experiments. The recombination effected in the gaseous phase follows an exponential law (experiments 6 to 8). The volume changes measured in experiments 1 to 3 are the differences between decomposition in the water phase and recombination in the gas phase. They also obey the same exponential law. It follows that the decomposition in the water phase must also follow that law. The data are still insufficient to calculate the ratio in which the emanation divides itself between gas and water. It is necessary first to find some method of determining the extent to which surface plays a part in the reaction. The data of the first three experiments, however, indicate that, volume for volume, the emanation produces a far greater effect in the liquid phase than in the gas phase.

The causes underlying these changes will be discussed at the end of this paper (pp. 990, 992).

Some rough measurements have been made of the total volume of electrolytic gas obtained from the solution of radium bromide containing 0·231 gram of radium as metal. The results are tabulated:

Time of collection in hours.	Volume of gas in c.c.	Volume per gram Ra per 100 hours.
22	7·5	148
70	20·0	123
94	26·4	122

It seems that there is gradual increase of recombination in the gas phase, as the amount of emanation in that phase increases. The corresponding figure, 60 c.c., calculated from results already published (Trans., 1907, **91**, 934: mean result, 32 c.c. per gram of radium bromide, $RaBr_2,2H_2O$), is quite different. Here, again, it appears that surface plays a considerable part in the amount of reaction.

Experiments with the Oxides of Carbon.

These can only be regarded as preliminary and qualitative.

Experiment 1.—Four days' accumulation of electrolytic gas and emanation from 0·231 gram of radium (metal) as bromide, allowed to decay during one day, was exploded down; the residual gas was mixed with a small quantity of carbon dioxide, and cooled to −185° by means of liquid air; the hydrogen was then removed by pumping. After the temperature had risen, the carbon dioxide and emanation were forced into a small measuring tube (capacity, 0·1197 c.c.) and readings taken. It was thought probable that the dioxide would decompose into carbon monoxide and oxygen, and that the increase of volume would be measurable. On the contrary, the gas contracted very slightly in volume (from 0·0907 to 0·0870 c.c. in three days), and a black ring of carbon began to deposit immediately, just above the mercury surface. After the third day, no readings could be made, on account of this carbon deposit, and at the same time owing to the formation of an appreciable quantity of mercuric oxide at the mercury surface.

Experiment 2.—Four days' accumulation of emanation, from 0·2307 gram of radium (metal) as bromide, was separated as previously, and used to treat a much larger quantity of carbon dioxide. An exactly similar result was obtained. A ring of carbon above the mercury surface was distinctly noticeable before the end of the first day, and gradually increased in thickness. The volume slowly decreased (in three days from 0·592 to 0·581 c.c.). The gases were afterwards pumped off, pure oxygen introduced, and the tube heated to 300—400°. The carbon burned away quietly, the volume remaining unchanged. The tube was broken before the carbon dioxide could be measured.

Experiment 3.—Carbon monoxide was prepared from formic acid and sulphuric acid. It was introduced into the apparatus in the usual manner, emanation and oxygen being added (the experiment was one of three conducted simultaneously). The emanation was equivalent to 0·05 E. The gas immediately commenced to contract, and carbon was deposited. Readings were taken over a period of four weeks.

Time in days.	Pressure in mm.	Volume in c.c.	$V_t - V_\infty$.	$Q = 100\dfrac{V_t - V_\infty}{V_0 - V_\infty}$.	log Q.
0	299·2	1·046	0·177	100	2·000
0·02	300·1	1·048	0·179	101·1	
0·04	300·9	1·051	0·182	102·8	
0·06	299·7	1·047	0·178	100·6	
0·07	298·9	1·044	0·175	98·9	
0·09	298·1	1·042	0·173	97·7	
0·11	297·1	1·038	0·169	95·5	
0·21	296·2	1·035	0·166	93·8	
0·25	296·1	1·035	0·166	93·8	1·972
0·29	297·1	1·038	0·169	95·5	
0·81	290·7	1·010	0·141	79·6	1·901
0·92	289·0	1·006	0·137	77·4	1·889
1·89	281·1	0·981	0·112	63·3	1·801
2·80	275·1	0·959	0·090	50·8	1·706
3·81	272·1	0·949	0·080	45·2	1·655
4·81	266·1	0·928	0·059	33·3	1·522
5·81	262·1	0·914	0·045	25·4	1·405
6·81	260·4	0·908	0·039	22·0	1·342
10·07	258·6	0·901	0·032	18·1	1·258
14·84	252·7	0·880	0·011	6·2	0·792
19·88	253·8	0·884	0·015	8·5	0·929
23·84	250·3	0 872	0·003	1·7	0·230
26·80	249·7	0·869	0·000	0·0	

The gas was pumped off and analysed:

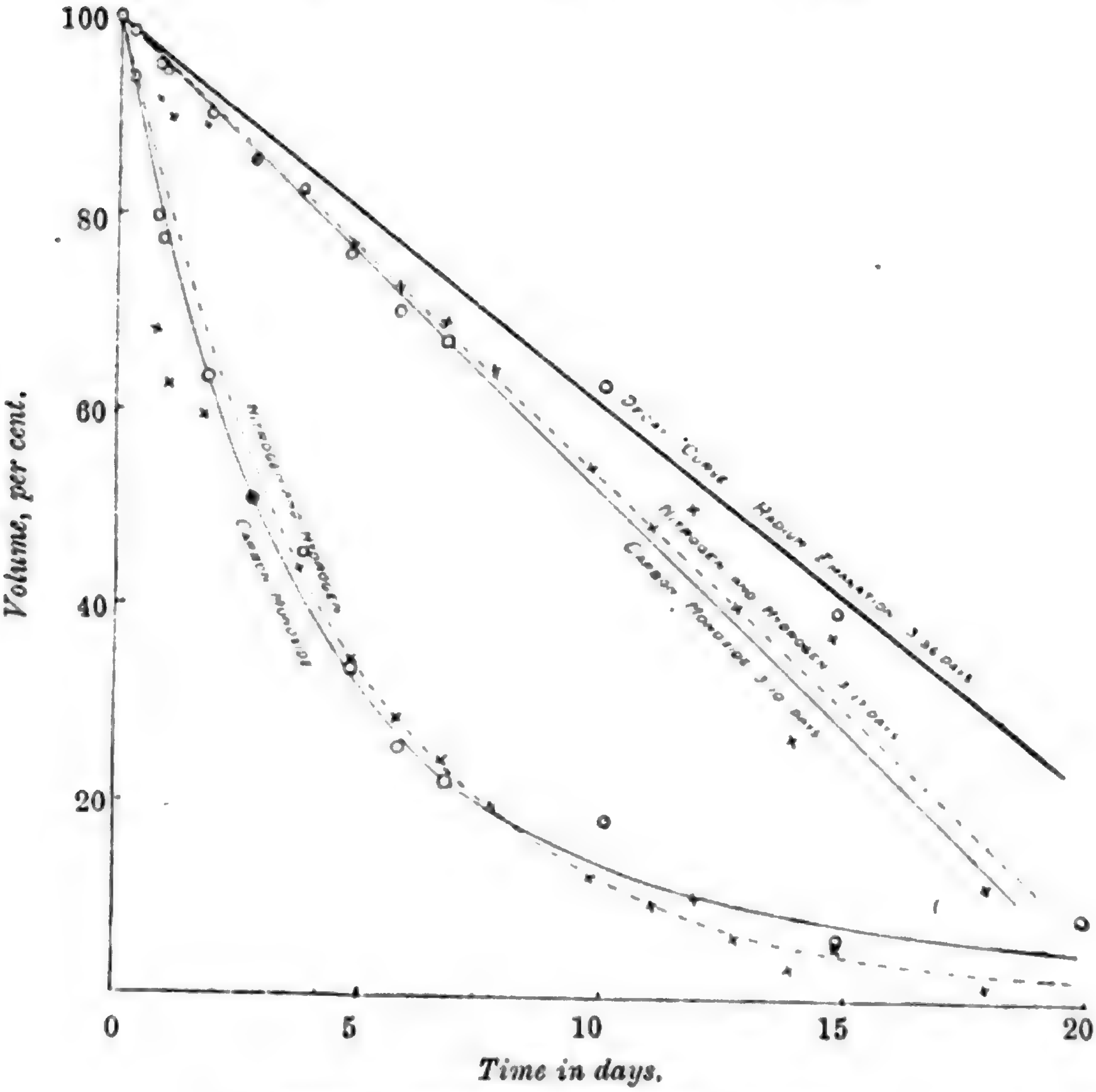
Carbon dioxide	0·084	c.c.
Oxygen	0·041	,,
Carbon monoxide	0·755	,,
Total volume	0·880	,,

Apparently, therefore, the monoxide decomposed to form both carbon and oxygen, and carbon and carbon dioxide, although it is possible that the carbon dioxide was produced by the interaction of the oxygen and carbon. The curves are shown in Fig. 7; the time of half change was 3·1 days.

Experiment 4.—It was considered possible that, if yellow phosphorus were present when carbon dioxide was treated with emanation, the oxygen would be absorbed as fast as formed, and the rate of reaction thereby rendered measurable. The experiment was performed in a tube of the form *D*, Fig. 2, the tube being sealed to the apparatus, and phosphorus introduced through the side-tube, which for that purpose was made specially long and wide, and which was then sealed. Absolutely pure carbon dioxide was introduced in the customary manner, and emanation with oxygen added. The phosphorus was gently warmed, and immediately on melting, part catching fire and absorbing the oxygen present, completely changed to the red variety. Although it has been observed (Becquerel, *Compt. rend.*, 1901, **133**, 709) that β-rays change yellow into red phosphorus, such immediate action was not expected.

A series of readings was taken, and it will be observed that there was a slight increase in volume. The emanation used was equivalent to 0·125 E.

Time.	Pressure.	Volume.
0	405·6	1·828
0·75	411·0	1·894
1·66	420·3	1·937
1·75	425·8	1·963
2·66	426·7	1·968
6·0	429·4	1·980
15·71	417·6	1·925*



⊙ Points in experiment with carbon monoxide.
× Points in experiment with nitrogen and hydrogen.

FIG. 7.

The gas was analysed, with the following result:

Carbon dioxide......	1·400 c.c.
Carbon monoxide..................	0·498 ,,
Oxygen	0·027 ,,
Total volume......	1·925 ,,

---

* This reading was probably incorrect, the apparatus having been moved in the interval.

It would appear, therefore, that with carbon dioxide, also, both possible reactions take place; the non-increase of volume in the first two experiments, and the increase in the last, point to some factor, as yet unknown, which determines the nature of the change.

Experiment with Hydrogen Chloride.

The hydrogen chloride was prepared from sodium chloride and sulphuric acid, and may have contained a trace of impurity. It was introduced into the measuring tube *A*, Fig. 2, in the usual manner, and emanation (0·069 E) and hydrogen introduced. The method of reading has been indicated previously (p. 968). The measurements follow. The volume of the measuring tube was about 6·6 c.c.

Time in days.	Volume in c.c.	$V_0 - V_\infty$.	$Q = 100\dfrac{V_t - V_\infty}{V_0 - V_\infty}$.	log *Q*.
0	2·464	0·561	100	2·000
0·017	2·454	0·551	98·2	1·992
0·73	2·204	0·301	53·4	1·728
1·93	2·086	0·183	32·6	1·513
2·73	2·079	0·176	31·4	1·496
3·75	2·060	0·157	28·0	1·447
5·80	2·038	0·135	24·1	1·381
9·77	1·985	0·082	14·6	1·165
13·78	1·949	0·046	8·2	1·914
18·76	1·930	0·027	4·8	1·682
23·86	1·926	0·023	4·5	1·649
25·76	1·903	0·000	0·0	

The curves are shown in Fig. 8. The time of half change is 5·9 days.

In considering these curves, it must be remembered that the errors of observation are much larger than usual, both volume and pressure readings being taken, and that the pressure readings varied only between the limits 511·4 and 594·3. The presence of mercurous chloride was observed after the first day, and a considerable amount was deposited during the experiment on the whole surface of the tube. The gas was analysed, and found to contain 0·322 c.c. of hydrogen. This does not agree very closely with the calculated value. The actual final volume was 1·993, the difference, 0·090, was due to bubbles from the tap, added in the course of the experiment, and probably consisting of carbon dioxide.

Experiments with Ammonia and with Nitrogen and Hydrogen.

The first experiment was performed in a simple measurement tube (type *C*, Fig. 2). Ammonia, prepared from slaked lime and ammonium chloride, was introduced as usual. Hydrogen and emanation (0·060 E) were added. The initial decrease in volume recorded below demanded attention. The remaining experiments were performed, therefore, in a specially devised apparatus, shown in Fig 3. The method of using this has been described (p. 969). In the second experiment, the presence of a trace of moisture along with the gases was observed. This was thought to account for the initial decrease found in that case. In the third experiment, especial precautions were taken to dry the apparatus and purify the gas. The initial decrease in volume was almost eliminated. In order to compare the results, the initial volume has been taken as zero; in all cases the corresponding numbers are shown in the fourth column. In the second and third experiments, the respective quantities of emanation employed, in each case added with hydrogen, were 0·24 E and 0·23 E.

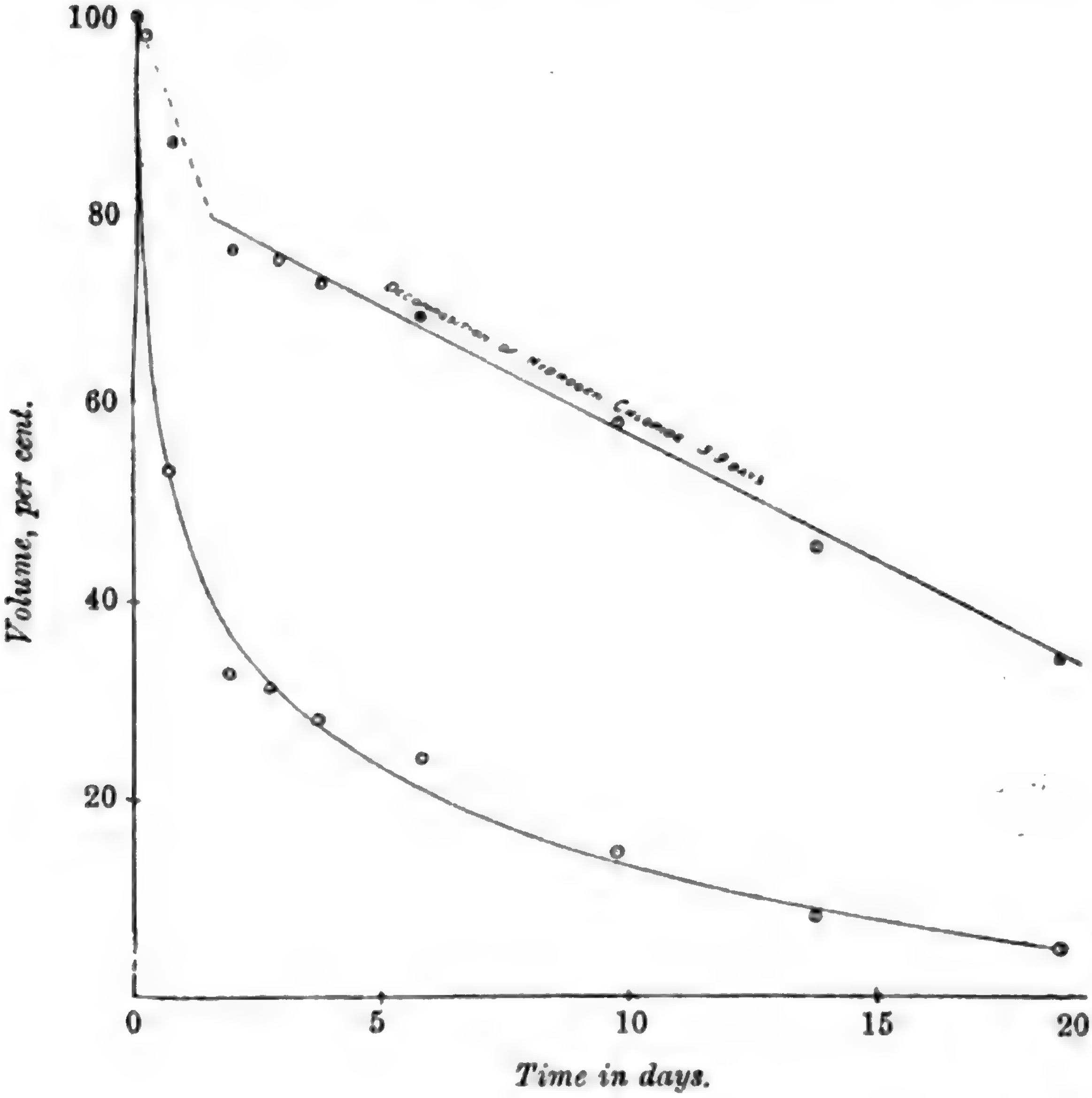


FIG. 8.

Experiment 1.—

Time.	Pressure.	Volume.	Arbitrary scale.	$V_\infty - V_t$.	Q.	log Q.
0	551·4	0·628	0	—	—	—
0·17	546·1	0·622	–0·006	—	—	—
0·73	485·6	0·553	–0·075	—	—	—
1·93	461·8	0·526	–0·102	0·046	100	2·00
2·73	469·7	0·535	–0·093	0·037	80	1·90
3·75	481·2	0·548	–0·080	0·024	52	1·72
5·80	491·7	0·560	–0·068	0·012	26	1·42
9·77	496·0	0·565	–0·063	0·007	15	0·82
13·78	499·6	0·569	–0·059	0·003	11	0·04
18·76	502·2	0·572	–0·056	0·000	0	—
23·86	502·0	0·572	–0·056			

Experiment 2.—

0	425·7	1·026	0
0·81	396·5	0·956	–0·070
1·74	431·7	1·040	+0·014
2·75	510·0	1·229	+0·203

Experiment 3.—

0	807·1	1·945	0			
0·18	805·3	1·941	–0·004	0·429	100	2·000
0·90	828·3	1·996	+0·051	0·374	87·2	1·940
1·90	864·7	2·084	0·139	0·286	66·7	1·824
2·18	883·0	2·128	0·183	0·242	56·4	1·751
2·92	911·0	2·195	0·250	0·175	40·8	1·610
4·90	942·4	2·271	0·326	0·099	23·1	1·363
6·91	964·4	2·224	0·379	0·046	10·7	1·030
10·05	974·2	2·348	0·403	0·022	5·1	0·710
11·90	979·0	2·360	0·415	0·010	2·3	0·367
∞		(2·370)	(0·425)	0·000	0·0	—

The curves obtained by plotting the figures in column 4 against time are shown in Fig. 9. In order to see whether those in experiments 1 and 3 are exponential (in experiment 3, the final value was found by extrapolation), the first value in column 5, showing increase in volume, was taken at 100, logarithms being obtained and plotted as usual (columns 6 and 7). The results are also shown in Fig. 9. They lie fairly closely on a straight line. The period of half action is, however, very different from 3·86 days, being 2·0 days for experiment 1 and 1·4 days for experiment 3.

The gases in experiment 2 were transferred to a tube over mercury, and allowed to stand for some weeks; they were finally analysed. Those in experiment 3 were passed back into the burette (*C*, Fig. 3), and analysed immediately. The gas in experiment 1 was also analysed.

Experiment.	Nitrogen.	Hydrogen.	Hydrogen added initially.
1	0·421 c.c.	trace	0·191 c.c.
2	0·502	0·660	0·090
3	0·249	0·846	0·222

The considerable, but decreasing, discrepancy between the measured and the calculated amounts of hydrogen corresponds with the known presence of traces of moisture. It is possible that in each case a trace of air was admitted, either as impurity in the ammonia, or with the emanation, with consequent formation of water and absorption of ammonia (giving the observed decrease). This would also affect the nitrogen values, and may account for the great difference between the rate of the reactions and that of the decay of the emanation.

Decomposition of ammonia.

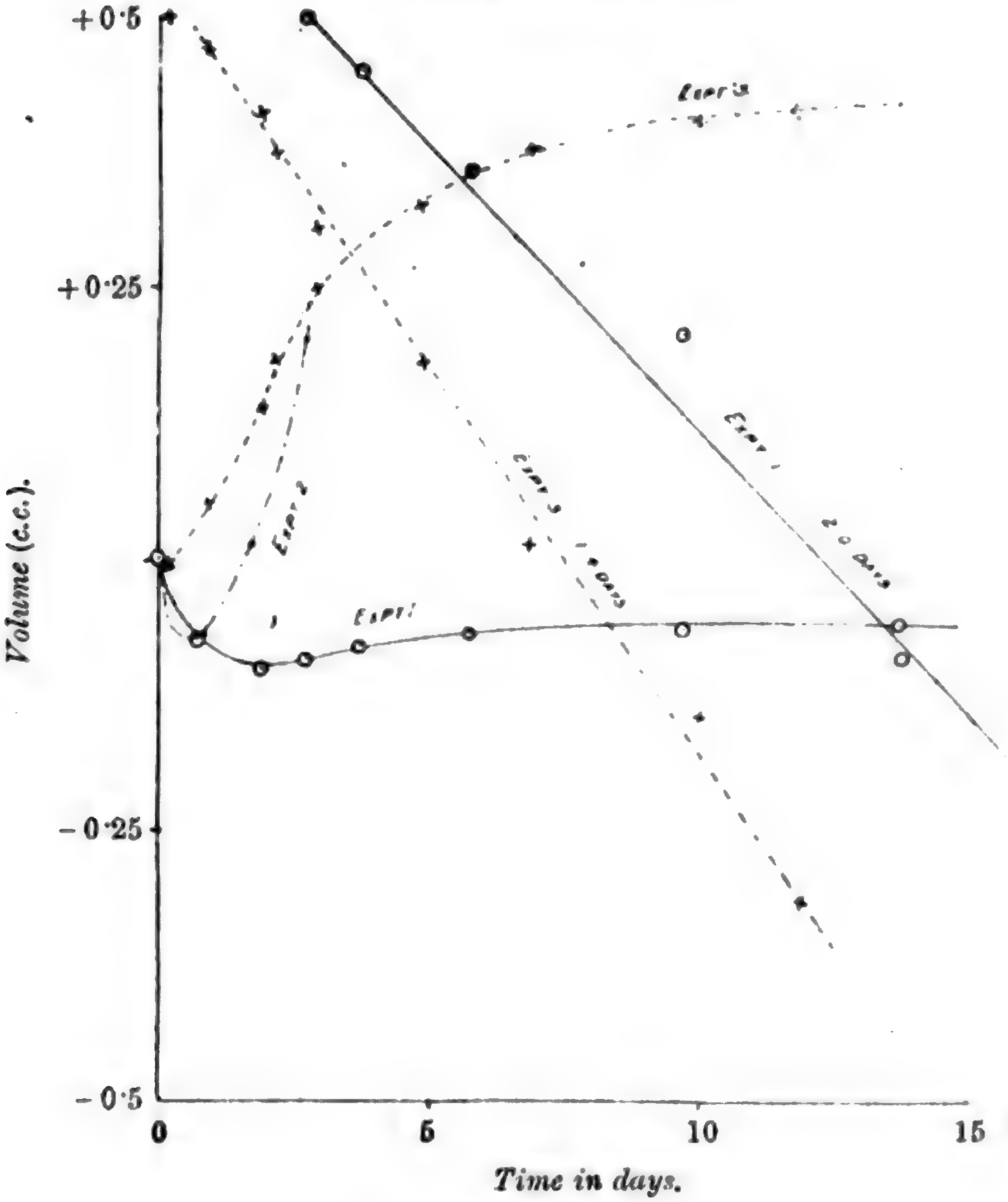


FIG. 9.

In a similar apparatus, containing some fused calcium chloride to absorb any ammonia that might be formed, a mixture of nitrogen and hydrogen was treated with emanation (0·239 E). The gases were prepared by sparking perfectly pure ammonia, the undecomposed ammonia being removed by dilute sulphuric acid. The emanation was added with excess of hydrogen. The results are shown below.

Time in days.	Pressure in mm.	Volume in c.c.	$V_t - V_\infty$.	$Q = 100\frac{V_t - V_\infty}{V_0 - V_\infty}$.	log Q.
0	745·6	2·256	0·236	100	2·000
0·005	743·8	2·250	0·230	97·4	
0·019	745·3	2·255	0·235	99·6	
0·08	751·5	2·273	0·253	108·0	
0·79	720·8	2·180	0·160	67·8	1·831
1·06	716·3	2·167	0·147	62·3	1·794
1·76	714·1	2·160	0·140	59·3	1·773
2·77	707·6	2·140	0·120	50·8	1·706
3·77	701·6	2·123	0·103	43·6	1·640
4·85	694·3	2·101	0·081	34·3	1·536
5·77	690·1	2·087	0·067	28·4	1·453
6·76	686·6	2·077	0·057	24·4	1·383
7·76	683·1	2·066	0·046	19·5	1·290
9·76	677·1	2·049	0·029	12·3	1·089
11·01	675·0	2·042	0·022	96·3	0·969
11·86	675·6	2·044	0·024	10·2	1·007
12·77	672·4	2·035	0·015	6·4	0·803
13·86	670·0	2·028	0·008	3·4	0·530
14·77	671·9	2·033	0·013	5·5	0·741
17·93	669·1	2·024	0·004	1·7	0·229
		(2·020)	0·000	0·0	

The curves are shown in Fig. 7; the time of half change was 3·17 days. Considering the small changes in pressure, and, in consequence, the larger percentage error, the approximation to an exponential curve is very good.

Experiments at 130°.

Experiment 1 (*Hydrogen and Oxygen*).—The electrolytic gases from the radium bromide solution, containing emanation corresponding with 0·263 E, were exploded, the emanation frozen at −185°, and the excess of hydrogen pumped off. Very pure electrolytic gas was then passed up over the frozen emanation, and, after the temperature had risen to air temperature, the gases and emanation were pumped off; carbon dioxide was removed by introducing a trace of potash. The gases were then introduced into an apparatus of the type shown in Fig. 1, and forced up into a small measuring tube, containing a point (volume at N.T.P., 0·1197 c.c.), and jacketed with chlorobenzene vapour. A series of readings were taken for nearly six hours. (The pressure has been corrected to 0°; the volume to N.T.P.)

Time in hours.	Pressure in mm.	Volume in c.c.
0·12	556·5	0·0877
0·28	557·6	0·0878
0·45	558·0	0·0879
0·62	556·1	0·0876
0·78	558·2	0·0879
0·95	560·4	0·0883
1·13	558·2	0·0879
1·27	558·1	0·0879
1·43	556·9	0·0877
1·60	554·9	0·0874
1·78	554·5	0·0873
2·05	553·5	0·0872
2·28	552·4	0·0870
2·52	551·4	0·0869
2·77	549·9	0·0866
3·08	547·7	0·0863
3·52	544·4	0·0857
3·83	542·6	0·0855
4·08	541·6	0·0853
4·35	540·2	0·0851
4·65	538·9	0·0849
4·92	535·6	0·0844
5·25	535·0	0·0843
5·58	533·1	0·0840
5·73	532·6	0·0839

The curve is shown in Fig. 10.

Experiment 2 (*Steam*).—A similar apparatus was used; the measuring tube was much larger (capacity, 1·287 c.c.). Platinum wires were fused through to act as a spark gap. The gases containing emanation (0·14 E) were sparked down to small volume, the remaining gas forced through a phosphoric oxide tube into the measuring apparatus, and, finally, a spark passed there, the flame being visible and proving the formation of steam. The mixture of steam and hydrogen was jacketed as usual, and readings were taken over a period of six hours. No expansion, such as would result from the formation of hydrogen and oxygen, was observed. On the contrary, a slight contraction took place. It was irregular, amounting in all to 3 per cent. of the total volume

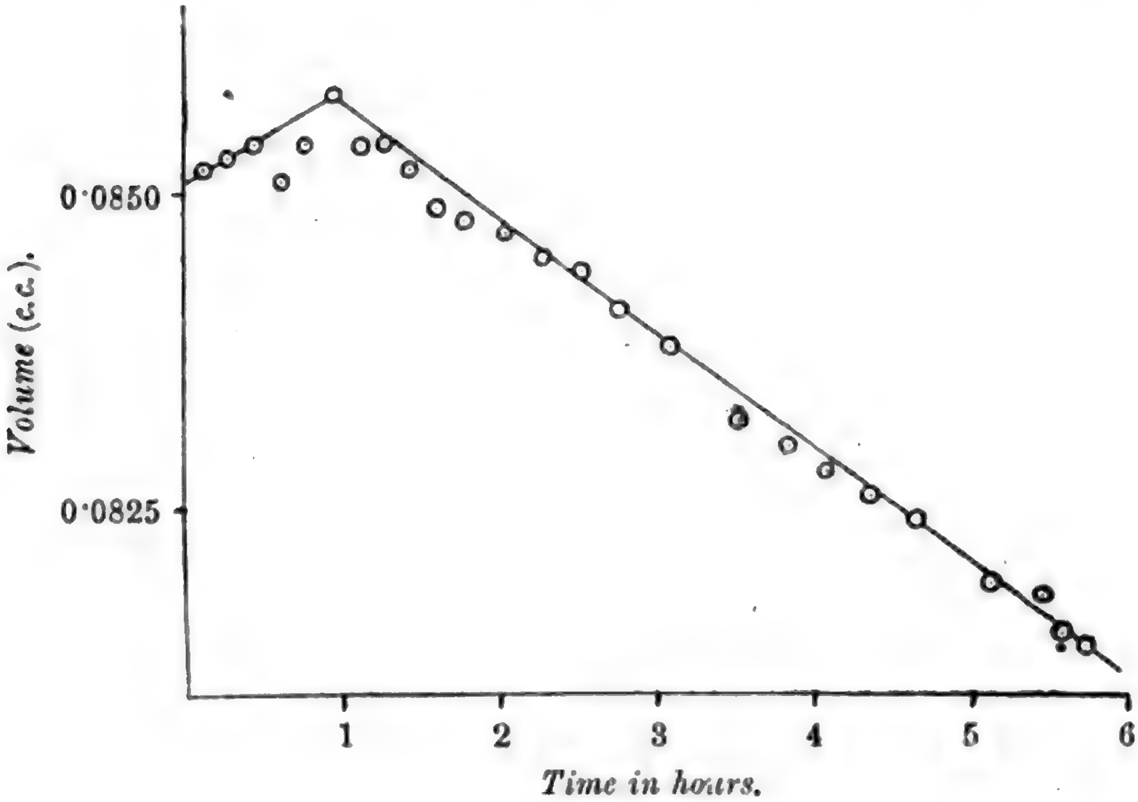


FIG. 10.

(0·425 to 0·414 c.c.), and may be perhaps accounted for by irregularity in the heating. The gas was allowed to stand at constant volume and air temperature overnight; on re-heating next day, it again varied in volume from 0·412 to 0·420 c.c. These measurements were repeated over several days, with similar results. The tube glowed brilliantly in the dark, and gradually became coloured, proving undoubtedly that emanation was present.

It must be concluded that the decomposition of steam by emanation is extremely small in amount, if any, and that the accuracy of measurement, certainly correct to 0·001 c.c., was not great enough to detect a change.

Neglecting, therefore, the decomposition of steam by emanation, it is possible to calculate the amount of recombination of electrolytic gas under the conditions of the first experiment. In 5·73 hours, $(0{\cdot}0883-0{\cdot}0839)\times 3$ c.c. $= 0{\cdot}0132$ c.c. had become converted into steam. The amount of emanation used was 0·252 E. If we presume that each particle of emanation in decomposing causes a certain definite volume of hydrogen and oxygen to combine, then 0·011 E has effected the combination of 0·0132 c.c. of gas, whence it follows that E will cause 1·2 c.c. of gas to combine. This is of a less order of magnitude than the figures obtained at ordinary air temperatures (compare experiments 6 to 8).

The Nature of the Chemical Change brought about by Radium Emanation.

We have already shown that whenever exact measurements have been obtained for water, hydrogen, and oxygen, the results give an exponential curve of half time approximating to 3·86 days, the period of half decay of radium emanation. We have pointed out that it would appear that each particle of emanation in disintegrating produces a definite quantitative chemical effect, since the amount changing at any time is proportional to the change of gas volume in that time. The rate of reaction of nitrogen and hydrogen, and of carbon monoxide, confirms these statements, although, in the latter, apparently several changes take place simultaneously. The question remains, in what manner are these chemical actions brought about? Many observers have studied the chemical phenomena produced by electrical energy applied in various ways. Thus a great number of chemical actions have been brought about by the silent electrical discharge, described in numerous papers by Berthelot and others. These treat chiefly of the production of organic compounds. Collie (Trans., 1901, **79**, 1063) has shown that a current at low pressure decomposes carbon dioxide very rapidly; under its influence oxygen and carbon monoxide recombine slowly.

Numerous researches have also shown that various chemical actions, such as the formation of ozone, the decomposition of ammonia, of nitrous oxide, and of carbon monoxide, take place under the action of ultra-violet light. In this connexion, the work of Chapman, Chadwick, and Ramsbottom (Trans., 1907, **91**, 942) may be consulted.

Strictly comparable with such phenomena are the numerous chemical changes produced by radium preparations enclosed in glass bulbs, and allowed to act by means of the rays penetrating the glass envelope, that is, the β-rays or electrons.

These have been found to have no action on water, or on mixtures of hydrogen and oxygen (Ramsay, *Meddel. K. Vet. Akad. Nobelinst.*, 1905, **1**, 909; Jorissen and Ringer, *Ber.*, 1906, **39**, 2093). They cause combination between hydrogen and chlorine (Jorissen and Ringer, *ibid.*), convert yellow into red phosphorus (Berthelot, *loc cit.*), and liberate iodine from hydriodic acid (Creighton and Mackenzie, *Amer. Chem. J.*, 1908, **39**, 474). The changes described in this paper are of the same nature,. but the degree of action is far greater. This is explicable on the assumption that the actions are brought about by α-particles. Their energy, as shown by their ionising power, is enormously greater than that of β-particles. The ionisation produced in gases by α-particles, or by cathode or X-rays, is supposed to be due to the gas particles obtaining an electric charge by collision, or by some other method. If we suppose that a mixture of hydrogen and oxygen is bombarded with α-particles, so that charged ions of both gases are produced, partial combination of hydrogen and oxygen is rendered certain. The effect of liberation of particles in water might be expected to be much greater; compare the effect of a charge of guncotton exploded in a confined and in an open space. The collision disrupts innumerable molecules of water, producing charged atoms of hydrogen and oxygen. Some of these recombine. The part that escapes recombination produces the changes in volume which are actually measured.

The experiments carried out at 130° do not altogether support this view. In the first place, it is well known that radium emanation itself gives off α-particles only, disintegrating into successive products, radium *A*, *B*, and *C*, of which the first and third give α-particles, and the second and third β-particles. The half life of these products is less than half an hour. During the first four hours after which emanation has been confined in any known space, the α-activity increases to almost three times the initial value. The amount of recombination of hydrogen and oxygen should increase similarly, if every α-particle produces a definite effect. But the curve in Fig. 10 is practically a straight line, and does not bear out that supposition. (The initial increase in the volume, reaching a maximum at the end of the first hour, seen in this experiment, and in those with electrolytic gas at air temperature, p. 977, with carbon monoxide, p. 982, and with a mixture of nitrogen and hydrogen, p. 988, seems to be due to the local increase in temperature set up by the emanation, which, even at 130°, imparts sufficient heat to the gas containing it to raise its pressure appreciably.)

Again, the action on steam should be analogous to that on hydrogen chloride, in which case decomposition was observed. But no action was noted. The only explanation which will bring this observation into line with the remainder, is the supposition that at the temperature of the experiment the reverse action is sufficiently rapid to cause any hydrogen and oxygen formed immediately to recombine. It must be remembered that the gas contained free hydrogen, the presence of which would increase the chances of recombination.

This paper has been wholly concerned with atomic changes. Whether, when the emanation produces these, some part of the energy is utilised in disintegrating the atoms of, say, carbon, or chlorine, according to the gas under observation, is a very different problem. For the present, we content ourselves with reiterating the chief conclusion reached in this paper, that *whenever radium emanation produces chemical action*, then, other conditions being unaltered, *each particle of emanation as it disintegrates produces the same amount of change.*

In conclusion, we desire to thank Professor A. W. Porter for his kindness in assisting us with the mathematical interpretation of these results.

UNIVERSITY COLLEGE,
LONDON.

XCIV.—*The Chemical Action of Radium Emanation. Part IV. On Water.*

By ALEXANDER THOMAS CAMERON and SIR WILLIAM RAMSAY, K.C.B.

IN the second part of this paper (Trans., 1907, **91**, 1593) an account was given of some experiments in which water and solutions of copper salts were treated with emanation, and the resulting products examined. It appears that, in presence of water, emanation disintegrates into neon; with copper solutions, into argon. There was some indication that minute traces of copper were transmuted into lithium, and possibly also into sodium. The experiments were carried out in bulbs of potash-lime and soda-lime glass. In order to minimise the possible errors, it was decided to repeat these experiments in silica. For this purpose, a bulb of very pure silica, of which the material had been boiled for half an hour before fashioning in order to remove alkalis by volatilisation, was obtained from Messrs. Johnson and Matthey.

It is convenient to describe the apparatus in this paper; it is being used in a series of experiments, the results of which will be communicated at a later date.

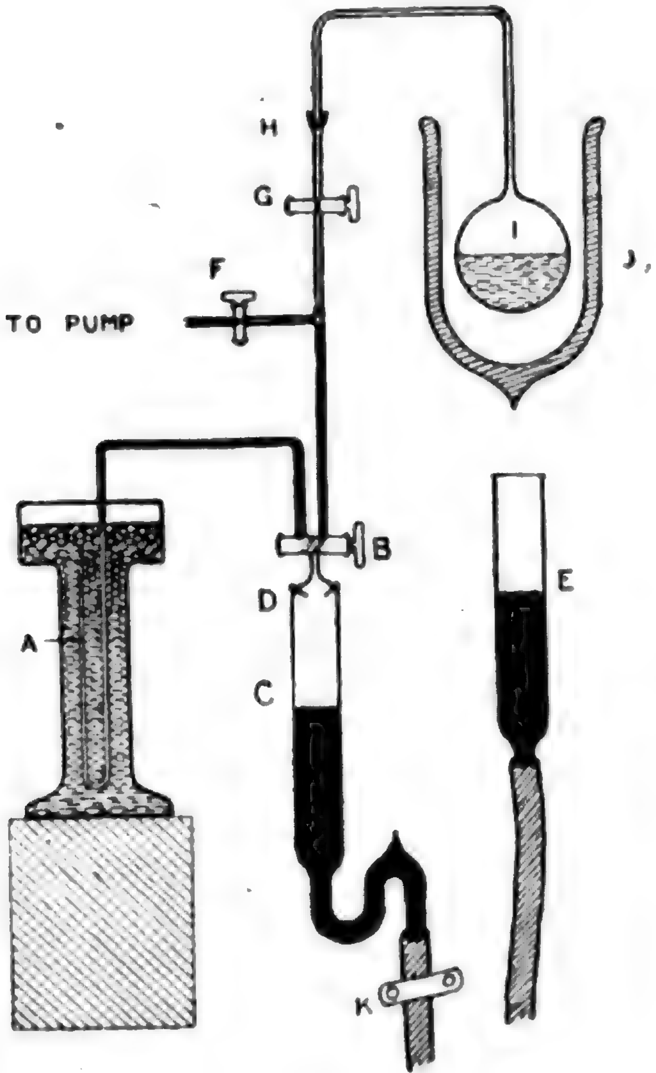


FIG. 1.

The silica bulb, *I*, Fig. 1, is half filled with the solution to be examined. It is then fixed to the apparatus by means of the ground-in joint, *H*, made air-tight with rubber grease. The apparatus is evacuated through *F* to below the stopcock, *B*. The emanation and electrolytic gas is introduced through the inverted syphon, *A*, as usual, into the burette, *C*, and exploded by means of the platinum electrodes at *D*. The rubber tube is clipped at *K*, *F* is closed, and *B* and *G* opened; the larger part of the emanation and excess of hydrogen enter the bulb. This is then jacketed with liquid air in the vacuum-vessel, *J*, and the mercury allowed to fill *C*, rising just above the stopcock, *B*, which is then closed. After a few minutes, in which time all the emanation condenses, and the solution in *I* freezes, *F* is opened, and the excess of hydrogen, with any helium present (formed from the radium bromide solution) is pumped off. *F* is then closed, and the mercury allowed to rise just above the ground-in joint, *H*. The tap, *G*, is closed, the mercury seal preventing any possible leakage.

It is usually desirable to add more emanation to the solution. The additions are conveniently made at intervals of three or four days. The following method has proved most suitable. The mercury below *G* is drawn down as far as possible into *C* by lowering the reservoir, *E*. The mercury surface is then fixed just below *D* by clipping the india-rubber tube, and the space above is completely cleared of any air leakage by pumping off through *F*. *G* is then opened. The gas in the bulb formed by the action of the emanation in the solution forces the mercury seal down into *C*. The bulb, *I*, is again jacketed with liquid air, and the emanation condensed along with the frozen solution. *F* is opened; the gas present is pumped off and stored. The fresh quantity of emanation is added as previously; the excess of hydrogen and the helium are again pumped off. A mercury seal is finally set above *H*, as before, and *G* is closed. This treatment is usually repeated four or five times, the final quantity of emanation being allowed to decay completely. The gas produced in each interval is added, and the total quantity finally analysed. The method of analysis has been given in detail previously (Trans., 1907, **91**, 1598—1599).

In the particular experiment described in this paper, two or three c.c. of pure water, prepared as described elsewhere (*ibid.*, p. 1601, foot-note), were used, the gas space above being somewhat greater. At the conclusion of the experiment, the water was transferred to a platinum dish and evaporated, the residue ignited, and weighed. The balance was accurate to one-fiftieth of a milligram. The actual weight found was 0·00001 gram. The residue was therefore within the error of weighing. The trace of residue was moistened and examined spectroscopically. Lithium was certainly absent, although the sodium line was visible. (The method can consequently be employed with some approach to accuracy with solutions of copper salts and those of other metals.)

The gas, when analysed, gave the following result:

Hydrogen	8·837 c.c.
Oxygen	3·509 ,,
Nitrogen and carbon dioxide	0·292 ,,
	12·638 c.c.

The nitrogen residue was examined for rare gases. The part not condensable in charcoal at liquid-air temperatures showed helium and neon. The helium yellow line was extremely intense, and the strongest neon reds had about two-thirds that intensity. This might be expected from the fact that the gas and water phases were approximately equal; the helium was produced in the gas phase. The spectrum was photographed twice; exposures were given of from six to seven minutes. The neon spectrum faded rapidly, and was barely visible during the second photograph. The results are shown in the accompanying plate (Fig. 2). *A* is the spectrum of pure helium, *B* that of the iron arc, *C* that of the second photograph (gases under examination), *D* that of the first, and *E* that of pure neon. The reproduction only shows some of the strongest red lines of neon in *C* and *D*. The helium and neon yellow lines appear as one thick line in the reproduction, although on the plate they are seen to be distinct.

The lines were read under a travelling microscope with the following results. The figures given under the heading of intensity are very roughly approximate, but show well the rapid disappearance of the neon spectrum.

Of the figures which follow, those printed in italics are known wave-lengths; where these only are given, they were chosen as points on the curve, from which the wave-lengths represented by figures in ordinary type were determined graphically. The figures following each symbol are the intensities as published:

Wave-length	*7065*	*6678*	6650	6600 *6599*	*6563*	6510 *6507*	6446
Intensity 1st photo...	2	10	—	1	3	2	—
Intensity 2nd ,, ...	1	10	0·5	0·5	10	1	0·5
Element..................	He5	He5	?	Ne4	H10	Ne6	?

Wave-length	6406 *6402*	6386 *6383*	6336 *6328*	6303 *6305*	6269 *6267*	6220 *6217·5*	6167 *6164*
Intensity 1st photo...	7	3	2	1	2	1	1
Intensity 2nd ,, ...	2	—	1	—	0·5	0	0
Element..................	Ne10	Ne8	Ne6	Ne8	Ne10	Ne8	Ne10

Wave-length	*6151*	6098 *6096*	6076 *6074·5*	6034 *6030*	5973 *5975*	5947 *5945*	5918
Intensity 1st photo...	3	2	1	1	1	2	1
Intensity 2nd ,, ...	1	0·5	—	0·5	0	0	—
Element..................	Hg9	Ne10	Ne10	Ne10	Ne6	Ne10	?

Wave-length	5904 *5903*	*5876*	5863 *5864*	5852 *5853*	5816 *5804*	*5790*	*5769*
Intensity 1st photo...	1	10	—	3	—	1	2
Intensity 2nd ,, ...	1	10	0·5	—	0·5	2	2
Element..................	Ne4	He10	? Hg2 H2	Ne20	? Hg2	Hg10	Hg10

Wave-length	*5461*	5338 *5341*	5330 *5332*	*5048*	5037 *5039*	5028 *5030*	*5016*
Intensity 1st photo	3	1	1	2	0·5	0·5	7
Intensity 2nd ,,	3	—	—	1	0·5	0·5	7
Element	Hg10	Ne4	Ne4	He2	Hsec.3	Hsec.3	He6

Wave-length	*4922*	*4861*	*4713*	4652 *4652*	4635 *4634*	4620	4600 *4598*
Intensity 1st photo	5	3	6	1	—	—	2
Intensity 2nd ,,	4	4	4	—	0·5	0·5	—
Element	He4	H20	He3	Hg5	H6	?	Hg5

Wave-length	4579 *4580*	4557 *4554*	4517 *4523*	4489 *4487*	*4472*	4461 *4461*	4449 *4448*
Intensity 1st photo	—	1	1	1	10	0·5	0·5
Intensity 2nd ,,	0·5	—	—	0·5	10	0·5	0·5
Element	H4	Hg6	Hg6	Hg8	He6	H5	H3

Wave-length	*4438*	*4388*	*4359*	*4348*	*4340*	4279 *4284*	4269 *4264*
Intensity 1st photo	1	5	6	1	2	4	1
Intensity 2nd ,,	1	3	6	1	4	—	—
Element	He1	He3	Hg10	Hg10	H15	Hg6	Hg8

Wave-length	4234 *4234·5*	4197 *4197*	4192 *4192*	4167 *4171*	*4144*	*4120*	4082 *4078*
Intensity 1st photo	2	2	0·5	0·5	1	2	0·5
Intensity 2nd ,,	—	—	—	—	0·5	1	1
Element	Hg6	Hg6	Hg5	H7	He2	He3	Hg10

Wave-length	4046 *4047*	*4026*	*3964*	3917 *3919*	*3888*
Intensity 1st photo	2	4	3	2	8
Intensity 2nd ,,	3	3	2	—	6
Element	Hg10	He5	He4	Hg7	He10

Of the unidentified lines, one only, 5818 (if corresponding with 5812), was observed in the previous experiment.

The spectrum tube was calibrated previously, and rough measurements were taken of the amount of gas present. The total volume (helium and neon) was approximately 0·8 c. mm. (not more than twice this figure, and not less than half).

In view of the slight leakage of air, stress cannot be laid on the presence of argon in the residual gases, although it was certainly present in reasonably large amount.

In carrying out such work, it is extremely difficult to prevent traces of air leaking into the apparatus during the considerable length of time which must elapse before an experiment is completed. Since 0·1 c.c. of atmospheric nitrogen contains sufficient argon to be detected spectroscopically after the nitrogen has been removed by sparking, the proof that the presence of argon is due to some other cause is rendered extremely difficult. Similarly, it is far from easy to free copper solutions completely from traces of lithium and to prove convincingly that lithium did not pre-exist in such solution treated with emanation. The detection of neon is open to no such objection. The only possible source, other than transmutation, is the aluminium of the electrodes. The vacuum tube had been previously run a great number of times at different pressures, washed out with air, and finally showed traces of hydrogen, and hydrogen alone. It is inconceivable that neon can have resulted thus by chance from two experiments with water, where in each case the residues were tested between those from numerous similar experiments with other solutions, in which no neon was detected. We must regard the transformation of emanation into neon, in presence of water, as indisputably proved, and, if a transmutation be defined as a transformation brought about at will, by change of conditions, then *this is the first case of transmutation of which conclusive evidence is put forward.*

ADDENDUM.

Since this paper was communicated, we have examined the accumulated residues of the gases pumped away from solutions of radium bromide, after removing hydrogen and oxygen by sparking, and the emanation in the usual manner. The heavier fraction was removed with charcoal cooled to liquid-air temperature. The lighter fraction consisted largely of helium. Neon was undoubtedly present; the spectrum was photographed, and many lines were conclusively identified. This might be expected, in view of the liquid phase provided by radium bromide solution itself.

The detailed results will appear later.

UNIVERSITY COLLEGE,
LONDON.

XCV.—*Molecular Volumes of the Nitrites of Silver, Mercury, and the Alkali Metals.*

By PRAFULLA CHANDRA RÂY.

THE nitrites of silver, mercury, and the alkali metals have engrossed my attention during the last twelve years, and their properties have been investigated from various points of view. Of late, I have been trying to gain an insight into their constitution, and it occurred to me that some additional light might be thrown on it by a comparative examination of their molecular volumes.

The investigation was carried on during the last two years, and, as the temperature of the laboratory varied from 21° to 31°, the determination of the specific gravities in benzene was found to be very troublesome, owing to its highly volatile character. Clear, transparent paraffin oil which had been carefully dehydrated answered the purpose much better. Owing to the viscosity of the oil there were, no doubt, some drawbacks to contend with, but they were surmounted by proceeding in the following manner. The finely-powdered salt being only partly covered with the oil, the bottle was given a gentle rotatory motion. The air bubbles in the interstices of the powder were thus driven out, although they remained suspended in the liquid. The bottle was then allowed to stand overnight in a desiccator. The next day the liquid became perfectly clear. The remaining portion of the bottle was then filled up as usual. In order to put to a crucial test the reliability of the method, pure samples of sodium and potassium chlorides, as also of potassium nitrate, were prepared and their specific gravities taken.

The specific gravity of sodium chloride at 27·6° was found to be 2·166; a sample of pure rock-salt, according to Sir W. H. Perkin, had the density 2·1675 at 6° (Trans., 1894, **65**, 20); the density at 15·5° is given as 2·155 by Clarke (*Constants of Nature*, 1st Supplement to Pt. 1, p. 9). The determination of the density of potassium chloride gave 1·996 at 21·9°; the mean of several observations by Quincke, Playfair and Joule, Filhol, Schiff and Schroder, and Kopp varies from 1·990 to 1·945. The specific gravity of sylvine is 1·990. Determination of the specific gravity of potassium nitrate gave 2·1064 at 26·4°; other observations on record are 2·096 to 2·108 at 4° (Playfair and Joule), and 2·109 (Retgers). It will be seen that as solids are far less expansible by heat than liquids, the divergence, due to the densities being taken at wide intervals of temperature, is almost negligible.

For test cases, the above three salts were purposely chosen, as they not only admit of a high degree of purification, but could be fused without decomposition. Salts which cannot be heated to fusion without risk of decomposition, for example, pentahydrated copper sulphate and anhydrous magnesium and copper sulphates, are liable to yield more or less discordant results (compare Thorpe and Watts, Trans., 1880, **37**, 103, 105, 106). It is necessary to remember that almost all the nitrites belong to this category.

Lithium Nitrite.—This salt was prepared by the interaction of silver nitrite and lithium chloride in presence of a small amount of water. The resulting hydrated crystals were left for a long time in a vacuum desiccator, when the anhydrous salt was obtained:

0·201 gave 0·2055 Li_2SO_4. Li = 13·03.

$LiNO_2$ requires Li = 13·22 per cent.

The specific gravity of several samples of distinct preparations was taken, and gave 1·706 at 31° and 1·636 at 27°. Mean = 1·671. Closer approximation could not be obtained.

Sodium Nitrite. (For method of preparation see Trans., 1905, **87**, 178.)—The specific gravity of a sample in benzene at 27° was 2·163; of another sample in the paraffin oil was 2·156 at 31·4°. A sample of Merck's, which was recrystallised twice (Found: Na = 33·38; $NaNO_2$ requires Na = 33·34 per cent.), gave 2·1508 at 20·4°, the mean of the several values being 2·157.

Potassium Nitrite. (For mode of preparation, compare *loc. cit.*, 178; Found: K = 45·93; KNO_2 requires K = 45·94 per cent.)—As the substance is deliquescent, it has to be handled with care. The determination of the specific gravity of one preparation gave 1·917 at 21°; that of a second preparation gave 1·919 at 23·7°. A sample of Merck's, purified by recrystallisation (K = 45·71), gave 1·909 at 23°. Mean sp. gr. = 1·915.

Silver Nitrite.—Some two dozen preparations were undertaken, the particular object in view being to see if there is any appreciable difference in the density of the nitrites as prepared simply by double decomposition between sodium nitrite and silver nitrate and the same when subjected to crystallisation (compare Rây and Gañguli, Proc., 1905, **21**, 280). It should be noted that, unless previously well dried, the nitrite cannot be heated in a steam-oven at 95—100° without slight decomposition; even a boiling solution of it evolves traces of nitric oxide, the decomposition proceeding according to the equation:

$$2AgNO_2 = AgNO_3 + Ag + NO.^*$$

Indeed, if pure silver nitrite be subjected to recrystallisation, the mother liquor, on evaluation, is found to yield a slightly higher value for the total nitrogen as compared with the nitritic nitrogen. The salts were drained free from the mother liquor and washed with cold water on the filter pump, and afterwards dried in a vacuum over sulphuric acid; they were finally powdered, sifted, and dried again. The determination of the specific gravity of the salt from double decomposition gave 4·451, 4·478, 4·543, 4·529 at 23—24·8°, whilst the specific gravity of the different samples from recrystallisation was 4·472, 4·462, 4·424 at 23—31°. It will thus be observed that no marked difference can be detected between the two sets of results. The mean of the last three values is 4·453.

Mercurous Nitrite.—As this salt can only be dried on a porous plate, it is invariably contaminated with traces of the adhering mother liquor. Three distinct preparations gave the specific gravity as 5·94, 5·876, and 5·96 respectively at 21—29°. The mean value is 5·925.

The molecular volumes of the nitrites are tabulated below for convenience of comparison:

---

* Hans Pick, "Beiträge z. charakteristik d. Nitrit-ions," *Inaug. Diss.*, *Breslau*, 1906, p. 27.

Salt.	Mol. wt.	Sp. gr.	Mol. vol.
$(LiNO_2)_2$*	106·02	1·671	63·44
$(NaNO_2)_2$	138·0	2·157	63·98
$(KNO_2)_2$	170·2	1·915	88·88
$(AgNO_2)_2$	308·0	4·453	69·16
$(HgNO_2)_2$	492·0	5·925	83·04

It will be observed that the specific gravity of the nitrites increases with the increase in molecular weight, the exception being in the case of the sodium compound. It is, however, well known that the salts of sodium are specifically heavier than the corresponding salts of potassium. It will further be seen that lithium and sodium nitrites have practically the same molecular volume. Potassium nitrite has the largest molecular volume in the series, but it is smaller than the atomic volume of the metal itself ($2K = 90·8$). As shown by Kopp long ago, the specific volumes of the salts of the alkalis and alkaline earths are often smaller than the atomic volumes of the component metals (Thorpe, *Kopp Memorial Lecture*, Trans., 1893, **63**, 800). Among the alkali metals, potassium is the most energetic and has the largest atomic volume,† and this property, as pointed out by Mendeléeff, is connected with the porosity (sponge-like structure) of the element. The group ·O·N:O, the radicle of the nitrite, penetrates into the interstitial space without causing any increase in bulk. The position of silver and mercury is somewhat anomalous (compare Trans., 1907, **91**, 2036). The comparatively small atomic volume of these metals is on a par with their inertness and feeble reactivity. The elements which constitute the radicle of the nitrite cannot insinuate themselves into the pores of the actual matter of the substance without at the same time contributing an appreciable accession to the bulk of the molecule. Further discussion on these points is reserved until later.

CHEMICAL LABORATORY,
PRESIDENCY COLLEGE, CALCUTTA.

XCVI.—*The Mutual Solubility of 2-Methylpiperidine and Water.*

By OTTO FLASCHNER and BASIL MACEWEN.

IT is impossible to draw many general conclusions as regards the influence of constitution on the mutual solubility of liquids, because only a very few members of any one homologous series are suitable for the determination of the complete solubility curve or even of one of the two critical solution-temperatures. An upper critical temperature with water has been observed in the following homologous series:

---

* The molecular weights have been doubled throughout because of facility of comparison with mercurous nitrite, which, there is reason to believe, has the formula $Hg_2(NO_2)_2$, and also with the nitrites of the alkaline earths.

† Cæsium and rubidium are, of course, left out of consideration for the present.

In the series of alcohols (Alexéeff, *Wied. Annalen*, 1886, **28**, 305):

*iso*Butyl alcohol	130°
sec.-Butyl alcohol	113·7°

In the series of aliphatic acids (Rothmund, *Zeitsch. physikal. Chem.*, 1898, **26**, 460):

n-Butyric acid	– 2·3°
*iso*Butyric acid	24·5°

The corresponding lower critical solution-temperatures, on account of the appearance of a solid phase, cannot be obtained.

On the other hand, in the following series, the lower critical solution-temperature can be determined, whilst the upper one lies too high for observation:

In the series of aliphatic amines:

Diethylamine (Guthrie, *Phil. Mag.*, 1884, [v], **18**, 499)	about 121°
Triethylamine (Rothmund, *loc. cit.*)	18·7°

In the pyridine series:

2 : 6-Lutidine (Timmermans, *Zeitsch. physikal. Chem.*, 1907, **58**, 144)	40°
2 : 4 : 6-Trimethylpyridine (Rothmund, *loc. cit.*)	6·42°

In the piperidine series (Flaschner, *Zeitsch. physikal. Chem*, 1908, **62**, 493):

1-Methylpiperidine	48·3°
1-Ethylpiperidine	7·5°

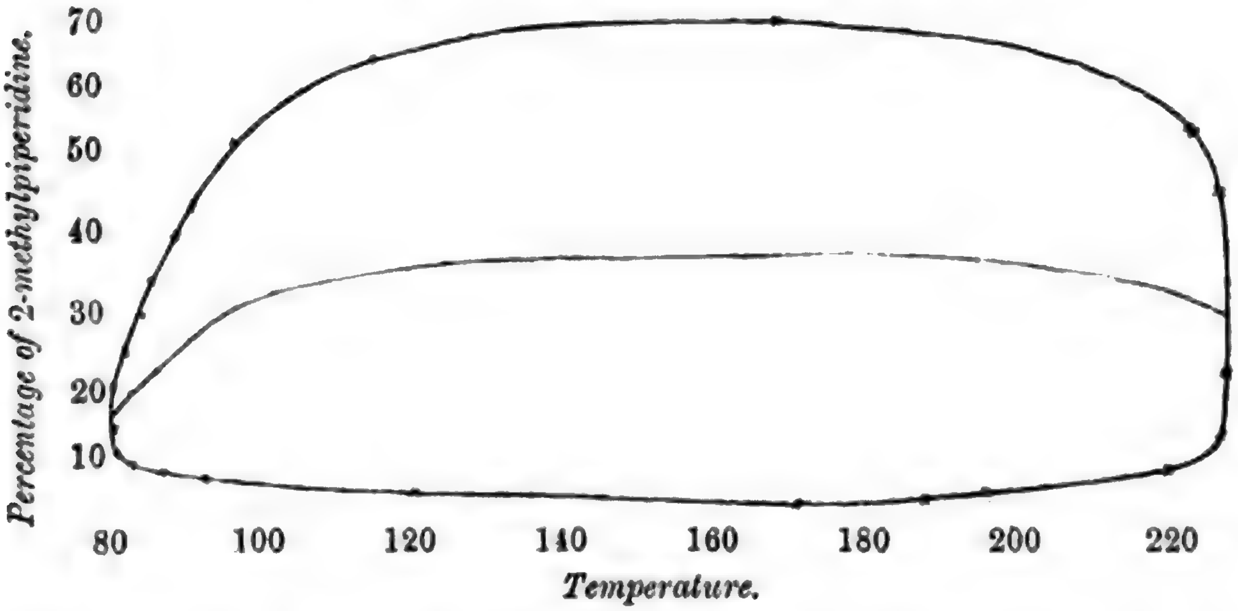
If, as suggested by Rothmund, the solubility of two not completely miscible liquids is represented by a closed curve, all these solubility rings of one liquid, for example, water when used in conjunction with the members of homologous series, seem to have the same "centre." The higher the member in the homologous series the less is the mutual solubility, and therefore the wider the theoretical ring, that is, the lower critical solution-temperature occurs at a lower point in the thermometric scale, and the upper critical temperature at a higher point (Timmermans, *Zeitsch. physikal. Chem.*, 1907, **58**, 145). From the examples given, it is evident that the increase of mutual solubility is due to the oxygen and nitrogen atoms, whilst, on the other hand, carbon and hydrogen atoms cause a decrease. The larger the carbon–hydrogen group attached to the oxygen or nitrogen, or the nearer such a group to these atoms, the smaller is the mutual solubility. A decrease in the number of carbon or hydrogen atoms produces an increase in the mutual solubility. α-Picoline is miscible with water in all proportions, whilst 2-methylpiperidine, which has six atoms of hydrogen more, is not miscible with water within certain limits of temperature. Considering that 1-ethylpiperidine is completely analogous to triethylamine and contains only one carbon atom more, one would expect a depression of the lower critical solution-temperature, and this is found to be the case, for the lower critical solution-temperature of the cyclic compound is lower by 11° than that of triethylamine. Therefore the ring formation itself can have little or no influence on the solubility.

Further, it appeared to be of interest to determine the influence of the position which an organic group in a cyclic compound occupies. As one of us has found that the piperidines form a class of substances which give with water an easily obtainable lower critical solution-temperature, and from the values of the dielectic constants (Ladenburg, *Zeitsch. Elektrochem.*, 1901, **7**, 816) other examples are to be expected, we have made determinations with 2-methylpiperidine. This substance was prepared according to Ladenburg's method (*Annalen*, 1888, **247**, 5). The fraction of commercial picolines boiling from 128° to 134° was purified by recrystallising the mercury salt, and the α-picoline was reduced with sodium and absolute alcohol. The 2-methylpiperidine obtained in this way was fractionated several times, and the single fractions were tested for purity by Crismer's method, by determining the lower critical solution-temperature. Finally, the fraction boiling at 117·5—118·5° was regarded as the purest, and was used for the following experiments.

The determination of the solubility curve was made by Alexéeff's well-known synthetic method. To determine the lower half of the curve, definite quantities of the base and water were introduced by means of a capillary pipette into a narrow tube, which was blown out at one end into a small bulb and at the other end drawn out into a capillary; the mixture was weighed. The capillary was sealed and the temperature was determined, at which separation into two layers took place; the capillary was then broken off, and, after a further quantity of the liquids had been added, it was used for another experiment. The determination of the upper half of the curve was carried out in small tubes of Jena glass (5 mm. external, 3 mm. internal diameter), drawn out into thick capillaries at one end. These liquid mixtures were only used for one determination, although even at 230° the glass was only slightly attacked by the base. In the following table, the amount of 2-methylpiperidine is given in percentage by weight of the solution. In the neighbourhood of the lower critical solution-point, a distinct critical opalescence was observed. The results are reproduced in the diagram.

2-Methylpiperidine.	Solution point.	2-Methylpiperidine.	Solution point.
72·3	165°	9·5	82·4°
64·7	112	8·6	86·5
52·4	94	7·8	92·4
47·0	88·8	6·8	homogeneous up to 170°
39·7	87	60·4	221°
33·7	87·2 opalescence	52·4	225
29·2	83 ,,	28·3	227
24·0	81 ,,	20·1	227
19·4	79·3	15·0	220
13·8	79·8	9·7	188
10·6	80·4	8·2	171

It is thus evident that the complete solubility ring of water–2-methylpiperidine can be followed; the only other case in which similar observations have been made is that of nicotine and water (Hudson, *Zeitsch. physikal. Chem.*, 1904, **47**, 113). The lower half of the curve has a shape similar to that of mixtures of 2 : 4 : 6-trimethylpyridine and of 1-methyl- and 1-ethyl-piperidine with water, namely, somewhat abruptly curved, whilst the upper nearly symmetrical half is similar to that of the known liquid pairs with upper critical solution-temperatures. Also, the law of rectilinear diameters, as Rothmund first showed, holds fairly well for the upper point, whilst the diameter for the lower part is sharply curved. The regularity indicated above is observed here also.. In consequence of the greater distance of the methyl group from the nitrogen atom in 2-methylpiperidine compared with 1-methylpiperidine, the lower critical solution-temperature of the former is increased by 31° and the upper one is depressed by about 60°.



We have to express our thanks to Sir William Ramsay for the kind interest taken in this research.

University College,
London.

XCVII.—*The Viscosity of Solutions.*

By CHARLES EDWARD FAWSITT.

THE work in this paper was carried out more than a year ago, and its publication was delayed in the hope that the measurements might be extended over a larger field. Being now fully occupied with high-temperature viscosity observations, I do not feel that any further delay is advisable, as it is not likely to result in a continuation of the work in the present paper, at any rate, in the immediate future.

The viscosity of aqueous solutions has already been discussed in previous papers (*Zeitsch. physikal. Chem.*, 1904, **48**, 585; *Proc. Faraday Soc.*, 1904, 664). When dilute solutions are studied, the viscosity is usually a linear function of the concentration of the solute. A number of colloidal aqueous solutions and some alcoholic solutions have now been examined, and it is found that they behave very similarly to aqueous solutions. It would have been of considerable interest to obtain viscosity measurements on colloidal solutions of metals and metallic sulphides, but an attempt to prepare such solutions in sufficient concentration to give viscosity measurements was not successful. Measurements of viscosity were, however, carried out with solutions of tungstic acid, hæmoglobin, gelatin, and albumen.

Measurements on alcoholic solutions here given are also in confirmation of the statement made in a previous paper (*loc. cit.*), that the viscosity of equimolecular solutions of substances forming a homologous series is to some extent an additive property.

EXPERIMENTAL.

Colloidal Solutions.—The tungstic acid used was prepared by dialysing a mixture of sodium tungstate and hydrochloric acid. The other substances were purchased in as pure a state as they could be obtained. The viscosity of gelatin solutions has already been investigated by Schroeder (*Zeitsch. physikal. Chem.*, 1903, **45**, 75), who noticed that the viscosity of such solutions depends greatly on their previous history. I have found that this property is not confined only to gelatin solutions, but appears to belong to other colloidal solutions, although in no case have I noticed the viscosity of solutions to vary in the extraordinary manner that gelatin solutions do, simply by allowing them to stand.

The following results were obtained at 25°, using the Ostwald form of U-tube with a glass capillary. The viscosity of water at 25° is taken as unity:

Substance.	Percentage.	Viscosity.	Substance.	Percentage.	Viscosity.
Albumen	0·25	1·019	Hæmoglobin	0·45	1·021
,,	0·85	1·066	,,	0·9	1·042
,,	1·70	1·140	Gelatin	0·0082	1·012
Tungstic acid	2·8	1·028	,,	0·0165	1·029
,, ,,	4·4	1·044	,,	0·033	1·096

The divergence from the linear formula is noticeable only in the case of gelatin. The Arrhenius formula $\mu = A^x$, where μ is the viscosity, x the concentration, and A a constant, is also unable to represent the case of gelatin solutions. Even among crystalloids, however, there are abnormal cases of this kind, as, for example, sucrose (Rudorf, *Zeitsch. physikal. Chem.*, 1903, **43**, 257).

Alcoholic Solutions.—The temperature of experiment was again 25°, and the viscosity of alcohol is taken as unity at this temperature.

Solutions in Ethyl Alcohol.

Substance.	Concentration.	Viscosity.	Substance.	Concentration.	Viscosity.
Butyramide	*N*/8	1·029	Methylcarbamide	*N*/8	1·028
,,	*N*/4	1·061	,,	*N*/4	1·050
,,	*N*/2	1·113	,,	*N*/2	1·099
,,	*N*	1·205	,,	*N*	1·212

The linear formula is applicable in both these cases.

A comparison of a number of amides at normal concentration gave the following results:

Acetamide	1·122	Valeramide	1·246
Propionamide	1·156	*n*-Hexamide	1·275
Butyramide	1·205		

The increment in the successive numbers is not constant, so that the property is not of a strictly additive character. The viscosity of the corresponding normal aqueous solutions (taking the value for alcohol again as unity) is as follows:

Acetamide	0·926	Butyramide	1·080
Propionamide	1·000	Valeramide*	1·149

* By extrapolation from more dilute solutions.

It will be noticed that the viscosity constants of the aqueous solutions increase more rapidly with substances of increasing molecular weight than those of the alcoholic solutions.

I have pleasure in expressing my thanks to the Council of the Chemical Society for a research grant to defray the expenses of this investigation.

THE UNIVERSITY,
GLASGOW.

XCVIII.—*A Criticism of Werner's Theory and the Constitution of Complex Salts.*

By JOHN ALBERT NEWTON FRIEND, Ph.D.

IN a recent communication (Friend, Trans., 1908, **93**, 260), a new theory of valency was suggested in which it was pointed out that the free valencies therein postulated correspond with the principal ones of Werner, and the latent with the auxiliary. There are, however, two important distinctions between the last named:

1. Whereas groups attached by the author's latent valencies are dissociable, those attached by Werner's auxiliary valencies are not.

2. Werner's auxiliary valencies differ from the principal ones in the amount of energy they contain, and it is regarded as possible for several of them to combine together to yield a principal valence.

The author's latent and free valencies, however, are practically identical, being separated from each other only because they are assumed to exist in pairs of equal and opposite sign, and thus do not affect the chemical nature of the atom to which they belong. In this respect they resemble the neutral affinities of Spiegel (*Zeitsch. anorg. Chem.*, 1902, **29**, 365) and the electrical double valencies of Arrhenius (*Theorien der Chemie*, Leipzig, 1906).

By adopting the author's theory, formulæ for simple and complex molecules can be obtained, which not only embody the advantages of Werner's system, but are free from many of its objections. This may be best shown by taking a few concrete examples.

Ammonium Chloride.

According to Werner's theory, the formula for ammonium chloride is:

$$H_3N....HCl,$$

where the dotted line represents the auxiliary valence joining the hydrogen to the nitrogen nucleus. The chlorine atom is thus free to dissociate, whereas the hydrogen is not. This formula explains the readiness with which ammonia and hydrogen chloride unite, and the ease with which the resulting compound dissociates on heating. Against it, however, a large number of facts may be arrayed. The nitrogen is here represented as quadrivalent and the hydrogen as bivalent, assumptions for which we have no warrant. The fourth atom of hydrogen is not attached to the nitrogen in the same way as the other three in Werner's formula, but the researches of Victor Meyer on the alkylammonium iodides indicate that no such difference in reality exists (Friend, *loc. cit.*, p. 268).

Further, if we replace hydrochloric acid by a weak acid, as, for example, acetic, the degree of dissociation of the weak acid is increased by neutralisation with ammonia. This, of course, should not occur if we are simply dealing with the addition of an NH_3-group to the hydrogen atom of the acid.

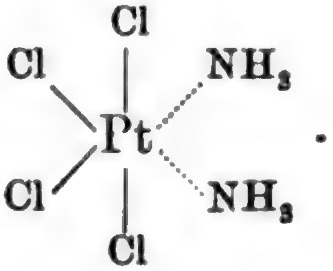
Finally, as Arrhenius (*loc. cit.*) points out, tetramethylammonium hydroxide, $(CH_3)_4N\cdot OH$, is a strong base, and its degree of dissociation is similar to that of the salts. According to Werner's theory, however, it is to be regarded as an additive product of trimethylamine and methyl alcohol, which latter is probably even less dissociated than water itself.

All these difficulties are overcome, however, if the present author's formulæ are accepted (*loc. cit.*, p. 267).

These schemes have the further advantage of explaining the observation of Kahlenberg, that union between ammonia and hydrogen chloride takes place in the presence of non-conducting benzene vapour, although, as Baker has shown (Trans., 1894, **65**, 612), when quite dry the two gases will not combine. Since the action is molecular, the benzene serves to bring the molecules together, the presence of an ionising solvent, such as water, being unnecessary.

Ammino-compounds.

Two compounds are known having the composition $PtCl_4(NH_3)_2$. Neither isomeride shows any appreciable dissociation in aqueous solution. It is therefore assumed by Werner that the six elements or groups are attached directly to the platinum, the four chlorine atoms by principal valencies, and the two NH_3-groups by auxiliary. Thus:

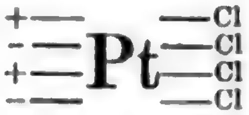


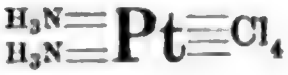
It is clear that if these groups are arranged spatially around the platinum atom, two different schemes are possible, namely, one in which the two NH_3-groups are adjacent, and one in which they are opposite. These represent the isomerides known.

Here, again, nitrogen is represented as quadrivalent, and the platinum as sexavalent. Further, the indefinite nature of the auxiliary valencies is a drawback, and it is difficult to see why the hydrogen and chlorine are not endowed with them here, as in so many other compounds.

Finally, if the fact that the elements are joined directly to the metal affords an explanation for the undissociable nature of the complex, it is remarkable that in potassium chloride, to quote a familiar example, we have a highly dissociable salt.

Spiegel (*loc. cit.*) suggests that the auxiliary valencies of Werner correspond with his neutral affinities. He therefore attributes to platinum four active valencies, by means of which the chlorine atoms are attached, and two pairs of neutral affinities (formula I):


(I.)



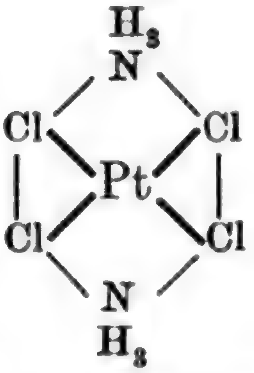
$\begin{matrix}H_3N\\H_3N\end{matrix}\!=\!Pt\!\equiv\!Cl_4$

(II.)

The ammino-compound under consideration would presumably be represented by the formula (II).

This certainly obviates the necessity of introducing quadrivalent nitrogen, and it also gives a certain definiteness to the auxiliary valencies. It does not explain the undissociable nature of the compound, however, and, further, if the neutral affinities of the metals generally exhibit such pronounced activity, it is remarkable that, both in solution and in a state of vapour, their molecules should be almost exclusively monatomic (Tammann, *Zeitsch. anorg. Chem.*, 1907, **55**, 289; Wartenberg, *Zeitsch. anorg. Chem.*, 1907, **56**, 320; Kurbatoff, *J. Russ. Phys. Chem. Soc.*, 1907, **39**, 1181, 1216).

The present author therefore suggests that a hexatomic shell forms round the metal in the way indicated by Werner, but that all the elements (or groups) are joined together by latent valencies, and not necessarily to the metal itself. Thus, in the case under consideration, the formula becomes:



NOTE.—For the sake of clearness the atoms are here, and in the succeeding schemes, represented as lying in one plane. It is easy to see that if a second pair of latent valencies is developed from each atom in the ring, a spatial configuration is obtained.

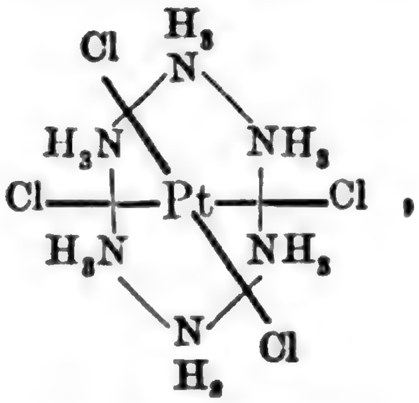
Whilst possessing none of the disadvantages of the formulæ of Werner and Spiegel, this scheme affords a ready explanation of the fact that dissociation cannot take place without the destruction of the complex.

If, now, the four chlorine atoms in the ring are replaced by ammonia, the complex $[Pt(NH_3)_6]Cl_4$ is obtained.

According to Werner, the six NH_3-groups are attached directly to the platinum, and constitute the first zone. The dissociable chlorine atoms hover round the nucleus in an indefinite manner, and are classed as the second or outer zone.

Briggs (Proc., 1908, **24**, 94) suggests that the platinum atom has both positive and negative affinities, and draws up a scheme according to which all ten elements (or groups) are attached directly to the metal.

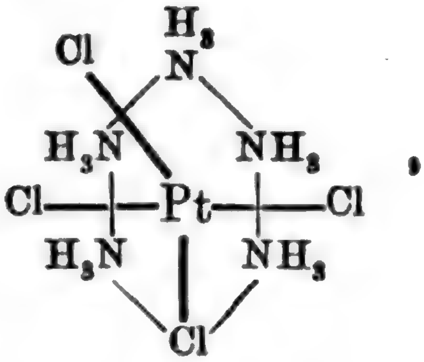
According to the present author, however, the complex is represented by the scheme:



in which the platinum retains its quadrivalent nature. The dissociable nature of the chlorine atoms is due therefore to *their being attached to the platinum atom, but not being included in the shell.*

It is easy to see by this arrangement that the complex $[Pt(NH_3)_6]$ will form one ion, for the platinum atom will be unable to escape from the hexatomic nitrogen shell surrounding it.

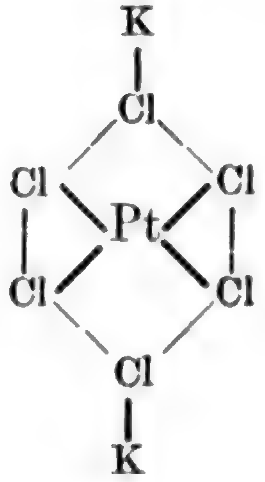
The formula for the complex $\left[\mathrm{Pt}^{(\mathrm{NH_3})_5}_{\mathrm{Cl}}\right]$ will thus be:



in which one chlorine atom has been included in the shell. Consequently, only three chlorine atoms are dissociable.

Other Complexes.

In potassium platinichloride, K_2PtCl_6, we have a typical example of a second class of complex, namely, that in which the simple ions are positive, and are attached directly to the shell and not to the central metallic atom. Thus:



By working along lines similar to these, it is easy to construct suitable formulæ for all the complexes which have as yet been discovered.

It is interesting to observe that inorganic compounds may thus be grouped into two classes, namely, those which contain hexatomic shells, and those which do not, whereas organic compounds are classified according as they possess hexatomic rings or not.

XCIX.—*The Reaction of Diazonium Salts with Mono- and Di-hydric Phenols and with Naphthols.*

By **Kennedy Joseph Previté Orton** and **Reginald William Everatt.**

Since the publication of Goldschmidt's (*Ber.*, 1897, 30, 670; *et seq.*) exact quantitative experiments on the coupling of diazo-compounds with anilines and phenols, it has been clear that there is little difference between the three classes, the diazonium salts, the diazotates (the "normal" or *syn*diazotates), and *iso*diazotates in this respect. Inasmuch as it was shown by him that only the hydrolysed fraction reacts with the phenol, the decisive factor in the rapidity and extent of the reaction is the degree of hydrolysis which the particular diazo-compound undergoes under the conditions. When other conditions (nature of the acid radicle, dilution, and temperature) are kept constant, this degree of hydrolysis depends on the strength of the diazonium base; or, with similar reservations in the case of the diazotates and the *iso*diazotates, on the strength of the corresponding acid, the diazohydroxide. Whether the free diazonium hydroxide, or whether the diazohydroxide (*syn*diazohydroxide) which Hantzsch claims to exist to a greater or less degree in solutions of all diazonium bases thus: $\begin{array}{c}\mathrm{Ar{\cdot}N{\cdot}OH}\\ ||| \\ \mathrm{N}\end{array} \rightleftharpoons \mathrm{Ar{\cdot}N{:}N{\cdot}OH}$, is the reactive substance, is immaterial for the present discussion. All circumstances which reduce the extent of this hydrolysis, such as excess of a mineral acid in solutions of diazonium salts, or excess of alkali in solutions of diazotates, diminish the rapidity and extent of the coupling. Inasmuch as the normal diazotates are generally the most hydrolysed of the three classes of diazo-compounds (when the three are obtainable), faintly alkaline solutions of this form are usually preferred for the preparation of the hydroxyazo-compounds.

No systematic study of the interaction of diazonium salts and phenols in which the constitution of the diazonium compound and the phenol has been varied appears as yet to have been made. That diazo-compounds couple with β-naphthol or resorcinol in the presence of mineral acid has been long known (Wallach, *Ber.*, 1882, **15**, 27; Liebermann, *Ber.*, 1883, **16**, 2859); and applications have been made of these observations in the colour industry. Bamberger and Hantzsch have used an alcoholic solution of β-naphthol for the preparation of the azo-compound from diazonium salts (for example, *Ber.*, 1895, **28**, 848). This method is alone available, and gives excellent results in the case of those diazo-compounds in which negative substituents are present in the positions 2, 4, and 6 with respect to the diazo-group, since such diazo-compounds will not couple in a solution which is more than feebly alkaline; moreover, in such feebly alkaline solutions halogen is eliminated from the benzene nucleus, and hence the preparation of a pure product is rendered difficult (Orton, Trans., 1903, **83**, 796; *et seq.*).

In our own experiments we have investigated the reaction of a series of diazonium salts of constitution varying between the highly basic diazo-ψ-cumene and the feebly basic *s*-tribromodiazobenzene, with a number of monohydric phenols, the dihydric phenols, and α- and β-naphthol.

All diazonium salts, even the diazonium hydrogen sulphates, couple with equal readiness with β-naphthol in alcoholic solution, both those derived from the feebly basic *s*-tribromobenzenediazonium hydroxide and similar bases, and those derived from the powerful bases, *m*-xylene- and ψ-cumenediazonium hydroxides. In fact, when the solid diazonium salts can be easily prepared, this method of obtaining the azo-β-naphthols is to be preferred.

The method of preparation is very simple. Molecular proportions of the diazonium hydrogen sulphate and the naphthol are respectively dissolved in so much alcohol that the diazonium salt is ultimately at a concentration of 1—2 per cent. Generally the separation of the azo-β-naphthol begins immediately, and is complete in a few minutes.

The melting point of the original separation is scarcely changed by recrystallisation from acetic acid.

Effect of Solvent.—Variation in solvent has very little effect on the coupling with β-naphthol. In methyl and ethyl alcohols, acetone, acetic acid, or formic acid, no differences were observed. When acetone was the medium, the diazonium salt was mainly in suspension. The low solubility of β-naphthol in water necessitated the use of a very large bulk of this medium, but the coupling of β-naphthol with *s*-tribromobenzenediazonium hydrogen sulphate was not in any way modified.

Nature of the Phenol.—The constitution of the phenol has a very marked influence on the reaction with diazonium salts. α-Naphthol is indistinguishable in its behaviour from β-naphthol, but the monohydric phenols of the benzene series scarcely react with acid solutions of diazo-compounds. Experiments were made with phenol, *o*- and *p*-cresol, *o*- and *p*-nitrophenol, using the series of diazonium salts mentioned above. At most a coloration was produced. It was shown in the case of *s*-tribromodiazobenzene, which reacts more extensively than the other diazo-compounds, that the normal product was formed. The replacement of the mineral acid by acetic acid, by addition of sodium acetate—in some cases considerable excess was necessary—of course induced combination.

The dihydric phenols, resorcinol and orcinol (quinol and catechol behave in an exceptional manner), resemble the naphthols. In an alcoholic medium, coupling is rapid and roughly quantitative with the hydrogen sulphates of all types of diazonium bases.

In water, in which solvent resorcinol and orcinol are readily soluble, there is differentiation. Coupling is only complete at the concentration, one per cent., and the temperature here used, with the diazonium hydrogen sulphates of bases containing negative groups, such as *s*-tribromodiazobenzene, *s*-tribromo-*m*-diazotoluene, and 3:5-dibromo-*p*-diazotoluene. All the other diazonium salts tried, such as those derived from bromoaniline, *p*-nitroaniline, aniline, *p*-toluidine, *m*-xylidine, and ψ-cumidine, either couple incompletely or do not react.

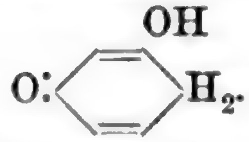
In these experiments the diazonium salt and the resorcinol (or orcinol) were dissolved in so much water that the diazonium salt was ultimately at a concentration of one per cent. After mixing, the solutions were kept for one hour, or in some cases three hours, the longer period not modifying the result materially. If the diazonium salt was unstable at the ordinary temperature, as was the case with the diazo-ψ-cumene, diazo-*m*-xylene, diazo-*p*-toluene, and diazobenzene, the mixture was kept at 0°, but with the more stable diazonium salts the solutions were at the ordinary laboratory temperature. The azo-compound was collected and the presence of unchanged diazo-compound looked for in the filtrate by reduction of the acidity by means of sodium acetate. In the first instance, one molecular proportion of sodium acetate was introduced, and any azo-compound which separated collected in half an hour, the filtrate being again mixed with another molecular proportion of acetate.

The diazonium hydrogen sulphates derived from *p*-toluidine, *m*-xylidine, 6-bromo-ψ-cumidine, and other similarly constituted diazonium salts, did not react at all with resorcinol until a molecular proportion of sodium acetate had been added, but this amount was sufficient to complete the coupling. That is, the coupling of these diazo-compounds is quantitative at the concentration used, in the presence of one equivalent of sulphuric acid. In the case of diazo-ψ-cumene no reaction had occurred even in the presence of two molecular proportions of sodium acetate, but after addition of a large excess a quantitative coupling results.

In the light of Goldschmidt's quantitative measurements, we may conclude that the phenol reacts most readily and extensively with those diazonium salts which are derived from the weaker diazonium bases, and are hence the more hydrolysed in the presence of a given concentration of acid. The weaker the base the more extensive is the coupling. As the coupling proceeds the concentration of the acid rises sufficiently in the case of *p*-nitrobenzene-, *p*-bromobenzene-, and benzene-diazonium hydrogen sulphates, to bring the reaction to a standstill. In the case of the other diazo-compounds above referred to, the initial concentration of acid does not permit any reaction.

The order of activity of a diazonium basis given by the reaction of resorcinol is the same as that deduced by Davidson and Hantzsch, and Engler and Hantzsch (*Ber.*, 1898, **31**, 1612, 2179; 1900, **33**, 2147), from measurements of the electrical conductivity. They found that ψ-cumenediazonium hydroxide was a base of the same order as the alkali hydroxides, and that diminution of the number of alkyl groups or accumulation of negative groups is followed by decrease in the activity of the base.

To what is to be ascribed the difference between the phenols in their behaviour is not easy to suggest. Goldschmidt showed that the reaction took place between the free phenol and the diazo-compound, but from his measurements, made mainly in alkaline solution, it is only possible to infer that the less acid phenols react more rapidly; for example, thymol reacted with the greatest speed with diazotates, excess of alkali having little deterring effect. Possibly the reactive phenols, naphthols, resorcinol, and orcinol (which belong to the more acid phenols) exist in solution to a small extent in an active tautomeric form. Other properties of these three phenols have suggested to chemists that they pass more extensively in certain solvents than other phenols into a quinonoid or ketonic form, thus:



If the diazonium or diazo-hydroxide reacts exclusively or more readily with this ketonic isomeride, the exceptional character of these three phenols would be in some degree accounted for.

The Influence of Concentration of Acid.—The solubility of resorcinol and orcinol in water renders easy a study of the influence of the concentration of acid on the coupling of those diazonium salts which couple completely under the conditions above described. A series of experiments was carried out in which the concentration of the acid (sulphuric acid) was continually increased, the concentration of the diazo-compound and the phenol being kept constant. The completion of the reaction was ascertained by collecting the product and diluting the mother liquor either with water or with aqueous sodium acetate.

In the case of 3 : 5-dibromo-*p*-toluenediazonium hydrogen sulphate a slight excess in the concentration of the acid was sufficient to bring the reaction to a standstill. Thus a solution of 0·5 gram of the salt in 40 c.c. of water coupled completely with one gram-molecular proportion of resorcinol present in the solution. But if a higher concentration of diazonium salt was used, for example, 0·85 gram in 40 c.c. of water, the coupling was partial, and only became complete on dilution with water.

With *s*-tribromodiazobenzene and *s*-tribromo-*m*-diazotoluene the results were very different. The concentration of the acid could be very largely increased without effect on the extent of the coupling. The former diazo-compound even reacted quantitatively with resorcinol in a 54·5 per cent. solution of sulphuric acid, the coupling only becoming slower and incomplete in a 73 per cent. solution. Nevertheless, even at this high concentration of acid only a small amount of diazo-compound remained uncombined. Similar results were obtained with the tribromodiazotoluene. Not only was the extent of coupling unaffected, but the rapidity was undiminished by the increase in the concentration of acid. Substitution of orcinol for resorcinol did not affect the results.

In a few experiments, methyl alcohol was used as a solvent instead of water. Up to a concentration of 7·7 per cent., the highest concentration used, sulphuric acid had no effect on the extent or rapidity of coupling. In this case, the extent of the coupling was demonstrated by collecting and weighing the coupled product, and not by dilution.

The identity of the azo-resorcinols formed in these acid media with those prepared and described in the foregoing in alcoholic or aqueous media in the absence of excess of acid was demonstrated by determination of melting points and by analyses.

The following tables will show a few of the experiments, and will give some idea of the procedure adopted:

1. s-*Tribromobenzenediazonium Hydrogen Sulphate and Resorcinol.*

Weight of diazonium salt.	Volume of H_2SO_4 in c.c.	Volume of solution in c.c.	No. of equivalents of H_2SO_4 to 1 equiv. of diazo-salt.	Percentage of H_2SO_4 by weight.
0·41	—	25	1	0·72
0·41	9·9	25	100	54·5
0·41	14·9	25	150	73·0

2. s-*Tribromobenzenediazonium Hydrogen Sulphate and Orcinol.*

0·41	—	25	1	0·72
0·41	1·9	25	20	13·5
0·41	2·9	25	30	18·8

3. s-*Tribromo*-m-*toluenediazonium Hydrogen Sulphate and Resorcinol*

0·42	—	25	1	0·72
0·42	2·9	25	30	18·8
0·42	4·9	25	50	31·0

The phenol and diazonium salt were used as aforesaid in molecular proportions. The depression of the solubility of the resorcinol by the sulphuric acid did not permit of higher concentrations of the reacting substances being used. The mixtures were maintained at the temperature of the laboratory, namely, 9—12°. The diazonium salts were colourless and in well formed crystals; they had been purified by solution in methyl alcohol and precipitation with ether.

A single experiment was made with benzenediazonium hydrogen sulphate and resorcinol. When these substances interact (in molecular proportions), the diazonium salt being at a concentration of 1 per cent., the coupling only takes place to the extent of 10·5 per cent. (estimated by weighing the azo-compound). When the concentration of sulphuric acid attains 2·3 per cent. no reaction is observed.

It is no easy matter to account for these remarkable observations. It is difficult to believe that in this case the reaction occurs between a hydrolytically dissociated fraction of the diazo-compound and the phenol; in 5—6 *N*-sulphuric acid, the concentration of hydroxyl ions must be so low that hydrolysis becomes impossible. These experiments add one more to the numerous recorded peculiarities of those diazo-compounds which possess these negative groups symmetrically placed with respect to the diazo-group. That this grouping entails some peculiarity in the constitution of the diazo-group, or in the constitution of the benzene nucleus, may be suggested, but further evidence must be collected before more definite views can be expressed.

The Coupling of Diazo-compounds and Resorcinol in Alkaline Solution.

Inasmuch as the conditions affecting coupling in alkaline solutions have been clearly defined by Goldschmidt, only a few experiments have been made with resorcinol to test the behaviour of some of the *s*-trisubstituted diazobenzenes. These diazo-compounds, *s*-tribromodiazobenzene, 3 : 5-dibromo-*p*-diazotoluene, 5-bromodiazo-*m*-xylene, &c., appear to yield only one series of diazotates, which are characterised by possessing considerable stability, resembling in many respects the *iso*diazotates of less substituted compounds.*

These various diazotates show considerable differences. In the first place, the behaviour of the *s*-tribromo-derivative is complicated by the insolubility of the potassium salt of the coupled product; this salt separates during the reaction, and thus prevents the free alkali hydroxide accumulating in the solution. On this account, the coupling is complete when molecular proportions of resorcinol and diazotate are used in absence of any excess of alkali. With the other two diazotates, no separation of an insoluble salt occurs, and the effect of the formation of alkali during the reaction can be studied, when due precautions are taken to prevent the entry of carbon dioxide from the air.

In a 1 per cent. solution, potassium dibromo-*p*-toluenediazotate only partly reacted with resorcinol. When the coupled product was filtered after keeping for three hours and carbon dioxide passed into the filtrate, a further separation of the azo-resorcinol resulted.

Under similar conditions, however, the bromodiazo-*m*-xylene completely reacted with resorcinol, but if initially one equivalent of sodium hydroxide were present, the coupling, although extensive, was not quite quantitative.

It is to be noted that, of the two diazo-compounds last mentioned, the bromo-*m*-xylenediazotate, which reacts most readily with the phenol, is consequently most hydrolytically dissociated, and therefore the derivative of a weaker acid, corresponds with a diazonium salt, which in its behaviour to resorcinol would seem to be derived from the stronger diazonium base. That constitution of the benzene nucleus which gives the stronger diazo-base yields the weaker diazo-acid.

---

* A number of diazotates of these symmetrical tri-substituted diazobenzenes have been prepared in this laboratory; their characters and peculiarities will be described in a subsequent communication.

Some Azo-phenols and -naphthols.

In the course of these experiments, we have prepared a number of azo-derivatives of resorcinol, orcinol, and α- and β-naphthol which have not hitherto been described.

Azo-derivative of Resorcinol.

The azo-derivatives of resorcinol can in general be easily prepared by mixing molecular proportions of diazonium salts, hydrogen sulphates or chlorides, and the resorcinol in aqueous or alcohol solution. In alcohol, the coupling is rapid and complete with all the diazonium salts, but in aqueous solution complete coupling only occurs when the diazonium salt is a derivative of a feeble diazonium base, that is, a base with negative constituents in the benzene nucleus. The addition of sodium acetate which causes the replacement of the strong mineral acid brings the interaction to completion. The diazonium salts derived from *s*-tribromoaniline, 3 : 5-dibromo-*p*-toluidine, and *s*-tribromo-*m*-toluidine interact quantitatively in aqueous solution notwithstanding the liberation of mineral acid during the process. In the case of the diazonium salts derived from aniline, *p*-bromoaniline, &c., the coupling is only complete after the addition of one molecular proportion of sodium acetate. With still stronger diazonium bases, such as those derived from the toluidines, *m*-xylidine, &c., no reaction takes place until a molecular proportion of sodium acetate is added, when, however, coupling is complete.

The azo-resorcinols are of course readily soluble in alkali hydroxides, and in many cases form potassium salts of singularly low solubility. These salts are precipitated when a dilute aqueous solution of resorcinol is added to dilute alkaline solutions of the diazonium compounds.

The azo-resorcinols (and azo-orcinols) which separate from aqueous solution, either acid or alkaline, are always in a colloidal condition. Filtering and pressing on an absorbent plate yields a material melting below 100°. This material may contain as much as 60 per cent. of water, which is slowly given up on exposure over sulphuric acid. No definite hydrates such as have been described by Hewitt were isolated.

s-*Tribromobenzene-4-azoresorcinol*, $C_6H_2Br_3 \cdot N_2 \cdot C_6H_3(OH)_2$, is prepared from *s*-tribromobenzenediazonium hydrogen sulphate and resorcinol in aqueous or alcoholic solution; it crystallises from glacial acetic acid as a pale red, microcrystalline powder melting at 182°:

0·2057 gave 0·2552 AgBr. Br = 52·8.

$C_{12}H_7O_2N_2Br_3$ requires Br = 53·18 per cent.

The *potassium* salt is an insoluble, gelatinous precipitate.

2 : 4 : 6-*Tribromo*-m-*toluene*-4-*azoresorcinol*,

$C_6HMeBr_3 \cdot N_2 \cdot C_6H_3(OH)_2$.

This compound is formed under exactly the same conditions as the last mentioned. It crystallises from glacial acetic acid in microscopic, pale orange crystals melting at 151—152°:

0·1853 gave 0·2236 AgBr. Br = 51·35.

$C_{13}H_9O_2N_2Br_3$ requires Br = 51·58 per cent.

3 : 5-*Dibromo*-p-*toluene*-4-*azoresorcinol*, $C_6H_2MeBr_2 \cdot N_2 \cdot C_6H_3(OH)_2$.—This substance was prepared as above described; it is best to use methyl alcohol as medium for the coupling.

The azo-compound crystallises from acetic acid in bright red needles melting at 141°:

0·22 gave 0·2087 AgBr. Br = 41·19.

$C_{13}H_{10}O_2N_2Br_2$ requires Br = 41·42 per cent.

p-*Bromobenzene*-4-*azoresorcinol*, $C_6H_4Br \cdot N_2 \cdot C_6H_3(OH)_2$, is prepared from the diazonium hydrogen sulphate and resorcinol in aqueous solution in the presence of one molecular proportion of sodium acetate, or from an alkaline solution of *p*-bromodiazobenzene and resorcinol when the potassium salt of the hydroxyazo compound separates. The compound crystallises from acetic acid in transparent, orange laminæ, which apparently contain acetic acid, since on washing with alcohol they become bright red and lose their transparency. It melts then at 191—192°, and is fairly soluble in alcohol or acetic acid:

0·1783 gave 0·1149 AgBr. Br = 27·42.

$C_{12}H_9O_2N_2Br$ requires Br = 27·24 per cent.

The *potassium* salt crystallises in large, red prisms, which are very sparingly soluble in water:

0·46 gave 0·1176 K_2SO_4. K = 11·48.

$C_{12}H_8O_2N_2BrK$ requires K = 11·82 per cent.

p-*Nitrobenzene*-4-*azoresorcinol*, $NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(OH)_2$.—This azo-compound, which appears to have been obtained by Meldola (Trans., 1885, **47**, 660), who gives no melting point, is formed as an insoluble sodium salt when an aqueous solution of sodium *p*-nitrobenzenediazotate is added to an aqueous solution of resorcinol. It is best purified by repeated recrystallisation from methyl alcohol, whereby a small amount of a high melting solid, possibly a bisazo-compound, is separated. It forms a dark red, microcrystalline powder melting at 199—200°:

0·1080 gave 14·6 c.c. moist nitrogen at 9·5° and 772 mm. N = 16·66.
$C_{12}H_9O_4N_3$ requires N = 16·25 per cent.

The *sodium* salt separates as a brownish-red, crystalline powder which is highly insoluble in water.

5-*Bromo*-m-*xylene*-4-*azoresorcinol*, $C_6H_2Me_2Br{\cdot}N_2{\cdot}C_6H_3(OH)_2$, is best prepared, using water as the solvent, for the diazonium hydrogen sulphate and the resorcinol. Crystallisation from acetic acid separated a small quantity of a material with a high melting point, above 250°, which is probably a bisazo-compound. The substance crystallises in red needles melting at 133°, and is readily soluble in methyl or ethyl alcohols:

0·2231 gave 0·1300 AgBr. Br = 24·79.
$C_{14}H_{13}O_2N_2Br$ requires Br = 24·09 per cent.

6-*Bromo*-ψ-*cumene*-4-*azoresorcinol*, $C_6HMe_3Br{\cdot}N_2{\cdot}C_6H_3(OH)_2$, is prepared by coupling the corresponding diazonium hydrogen sulphate and resorcinol in aqueous solution in the presence of sodium acetate. It crystallises from acetic acid in very dark red, lustrous needles melting at 214°, and is but sparingly soluble in alcohol:

0·1810 gave 0·1005 AgBr. Br = 23·64.
$C_{15}H_{15}O_2N_2Br$ requires Br = 23·85 per cent.

β-*Naphthalene*-4-*azoresorcinol*, $C_{10}H_7{\cdot}N_2{\cdot}C_6H_3(OH)_2$, was prepared from the diazonium salt and resorcinol in alcoholic solution, from which it separated in dark red needles melting at 181—182°. It crystallised readily from acetic acid:

0·1010 gave 9·3 c.c. moist nitrogen at 12° and 766 mm. N = 11·1.
$C_{16}H_{12}O_2N_2$ requires N = 10·63 per cent.

Azo-derivatives of Orcinol.

The behaviour of orcinol with diazonium salts very closely resembles that of resorcinol, the ready solubility of orcinol in water permitting the coupling to be carried out in that solvent. The reaction with diazonium hydrogen sulphates is quantitative in ethyl- or methyl-alcoholic solution; in water, the extent of the coupling depends on the character of the diazonium base in exactly the same way as was found in the case of the resorcinol, addition of sodium acetate often being necessary to bring the reaction to completion.

s-*Tribromobenzeneazo-orcinol*, $C_6H_2Br_3{\cdot}N_2{\cdot}C_6H_2Me(OH)_2$, crystallises from acetic acid as a bright red, microcrystalline powder melting at 199—200°:

0·1136 gave 0·1372 AgBr. Br = 51·39.

$C_{13}H_9O_2N_2Br_3$ requires Br = 51·58 per cent.

3:5-*Dibromo*-p-*tolueneazo-orcinol*, $C_6H_2MeBr_2 \cdot N_2 \cdot C_6H_2Me(OH)_2$, crystallises from a mixture of acetic acid and acetic anhydride in dull red needles melting at 179—180°, and is exceptionally soluble in methyl alcohol:

0·1511 gave 0·1414 AgBr. Br = 39·83.

$C_{14}H_{12}O_2N_2Br_2$ requires Br = 39·96 per cent.

p-*Bromobenzeneazo-orcinol*, $C_6H_4Br \cdot N_2 \cdot C_6H_2Me(OH)_2$, is best prepared by carrying out the coupling in alcoholic solution, and is separated from a small quantity of a solid of higher melting point by recrystallisation from methyl alcohol. It crystallises in long, bright red needles melting at 212—213°:

0·2129 gave 0·1326 AgBr. Br = 26·50.

$C_{13}H_{11}O_2N_2Br$ requires Br = 26·03 per cent.

5-*Bromo*-m-*xyleneazo-orcinol*, $C_6H_2Me_2Br \cdot N_2 \cdot C_6H_2Me(OH)_2$, is best recrystallised from methyl alcohol, whence it separates in bright needles melting at 192—194°:

0·2312 gave 0·1293 AgBr. Br = 23·80.

$C_{15}H_{15}O_2N_2Br$ requires Br = 23·85 per cent.

6-*Bromo-ψ-cumeneazo-orcinol*, $C_6HMe_3Br \cdot N_2 \cdot C_6H_2Me(OH)_2$, separated directly from the alcoholic medium, in which the coupling was carried out, in long, red needles, melting and decomposing at 214—215°:

0·2107 gave 0·1141 AgBr. Br = 23·04.

$C_{16}H_{17}O_2N_2Br$ requires Br = 22·89 per cent.

Azo-derivatives of α- and β-Naphthol.

2:4:6-*Tribromobenzeneazo-α-naphthol*, $C_6H_2Br_3 \cdot N_2 \cdot C_{10}H_6 \cdot OH$.—This compound is prepared by bringing together molecular proportions of *s*-tribromobenzenediazonium hydrogen sulphate and α-naphthol in methyl- or ethyl-alcoholic solution. The product separates immediately as a red, crystalline powder melting at 202°. From a mixture of acetic acid and acetic anhydride, it crystallises in red needles:

0·1978 gave 0·2306 AgBr. Br = 49·54.

$C_{16}H_9ON_2Br_3$ requires Br = 49·45 per cent.

p-*Chlorobenzeneazo-β-naphthol*, $C_6H_4Cl \cdot N_2 \cdot C_{10}H_6 \cdot OH$.

To prepare this azo-compound, *p*-chloroaniline was diazotised in alcoholic solution by means of amyl nitrite in the presence of three equivalents of sulphuric acid, an alcoholic solution of β-naphthol being added to the diazotised solution. The product separated as a dark crystalline precipitate melting at 159—160°; recrystallisation from acetic acid gave dark red needles melting at 160°:

0·2041 gave 0·1028 AgCl. Cl = 12·45.

$C_{16}H_{11}ON_2Cl$ requires Cl = 12·54 per cent.

The Reaction of Diazonium Salts with Quinol and Catechol.

The literature contains but little reference to attempts to couple diazo-compounds with quinol or catechol. Witt and Johnson (*Ber.*, 1893, **26**, 1909) state that diazobenzene and *p*-bromodiazobenzene give intense colorations with quinol in alkaline solution, but they neither isolated the product nor studied the reaction. Benzene- and *p*-toluene-azoquinol were obtained by them indirectly by coupling the monobenzoyl derivative of quinol with the diazo-compound.

We have investigated the action of a number of diazo-compounds, both as diazonium salts and as diazotates with quinol, in alcoholic and in aqueous solutions. The reaction is in all cases the same, a simple oxidation of the quinol, which behaves as a primary or secondary alcohol, thus:

$$Ar{\cdot}N_2{\cdot}OH + HO{\cdot}C_6H_4{\cdot}OH = Ar{\cdot}H + O{:}C_6H_4{:}O + N_2 + H_2O.$$

On adding a solution of the diazo-compound to the quinol, a momentary intense coloration appears, which becomes permanent when the whole of the diazo-solution has been introduced. The evolution of nitrogen begins immediately, even when the temperature is maintained at 0°. Considerable heat is evolved and the reaction may become violent. On addition of water to the alcoholic solution, a solid (or oil) is precipitated, the same material being deposited directly if water is used as the solvent. This solid (or oil) consists of the benzene derivative (benzene from diazobenzene, nitrobenzene from *p*-nitrodiazobenzene, *s*-tribromobenzene from *s*-tribromodiazobenzene, &c.), together with a very small quantity of a dark red solid of low and indefinite melting point. Quinone could always be detected by its odour and was isolated in several cases. When excess of quinol was used, quinhydrone was formed, and separated from the solution with the other substances.

So simple is this reaction of quinol with diazo-compounds that it may be recommended as a method of replacing the diazo-group by hydrogen. We did not observe any indications of the formation of the phenyl ethers of quinol.

With catechol the reaction is somewhat different. Witt and Mayer (*Ber.*, 1893, **26**, 1074) succeeded in coupling diazobenzene, *p*-nitrodiazobenzene, and *p*-diazotoluene with catechol. We find, however, that the highly-substituted benzenes, such as *s*-tribromodiazobenzene, &c., do not couple but oxidise the catechol, the reaction being similar to that with quinol.

In aqueous solution at 0°, the diazonium hydrogen sulphates of the stronger diazonium bases do not react with catechol, but on adding sodium acetate coupling takes place. With the weaker bases, in the same circumstances, reduction results.

UNIVERSITY COLLEGE OF NORTH WALES,
BANGOR.

C.—*Ethyl 6-Methyl-2-pyrone-3 : 5-dicarboxylate and its Derivatives.*

By JOHN LIONEL SIMONSEN.

DURING the course of his classical researches on the hydroxymethylene compounds, Claisen (*Annalen*, 1897, **297**, 10) showed that ethyl ethoxymethyleneacetoacetate condenses readily with ethyl sodioacetoacetate, and the product on acidifying yields ethyl diacetylglutaconate:

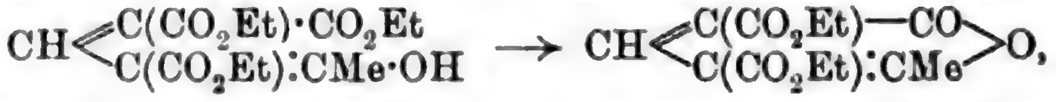
$$\mathrm{CO_2Et\cdot CAc{:}CH\cdot OEt + CH_2Ac\cdot CO_2Et} \longrightarrow \mathrm{CO_2Et\cdot CAc{:}CH\cdot CHAc\cdot CO_2Et + EtOH.}$$

As it seemed probable that ethyl α-acetyl*iso*aconitate,

$$\mathrm{(CO_2Et)_2C{:}CH\cdot CHAc\cdot CO_2Et,}$$

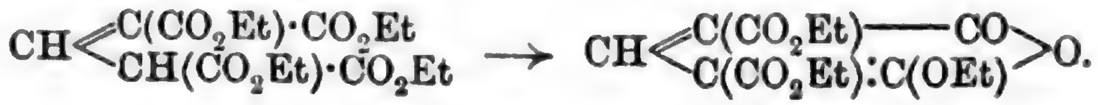
might result from the analogous condensation of ethyl ethoxymethylenemalonate with ethyl sodioacetoacetate, and as this ester was required for synthetical work in the terpene series, this condensation has been carefully investigated. Under the conditions given in the experimental part of this paper (p. 1026), condensation readily takes place, and the product of the reaction is a crystalline substance melting at 79·5°, which has the formula $C_{12}H_{14}O_6$, and is obviously derived from ethyl α-acetyl*iso*aconitate ($C_{14}H_{20}O_7$) by the elimination of alcohol.

The careful examination of the properties of this substance has conclusively proved that it is *ethyl* 6-*methyl*-2-*pyrone*-3 : 5-*dicarboxylate*, elimination of alcohol having taken place in the following way:



$$\mathrm{CH}<\begin{matrix}\mathrm{C(CO_2Et)\cdot CO_2Et}\\ \mathrm{C(CO_2Et){:}CMe\cdot OH}\end{matrix} \rightarrow \mathrm{CH}<\begin{matrix}\mathrm{C(CO_2Et)—CO}\\ \mathrm{C(CO_2Et){:}CMe}\end{matrix}>\mathrm{O},$$

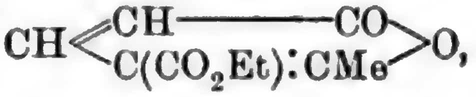
a change which is very similar to the conversion of ethyl dicarboxyglutaconate into ethyl ethoxycoumalindicarboxylate (Guthzeit and Dressel, *Ber.*, 1889, **22**, 1415):



$$\mathrm{CH}<\begin{matrix}\mathrm{C(CO_2Et)\cdot CO_2Et}\\ \mathrm{CH(CO_2Et)\cdot CO_2Et}\end{matrix} \rightarrow \mathrm{CH}<\begin{matrix}\mathrm{C(CO_2Et)——CO}\\ \mathrm{C(CO_2Et){:}C(OEt)}\end{matrix}>\mathrm{O}.$$

When ethyl 6-methyl-2-pyrone-3 : 5-dicarboxylate is hydrolysed with barium hydroxide or alcoholic potash, it is converted into a dibasic acid of the empirical formula $C_7H_6O_4$, the constitution of which has not as yet been definitely decided.

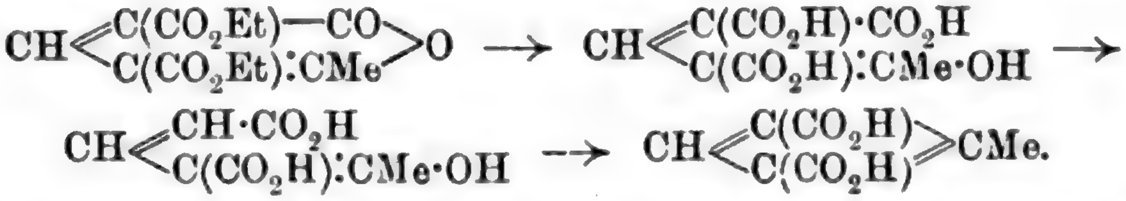
That this acid is not 6-methyl-2-pyrone-5-carboxylic acid,



$$\mathrm{CH}{<}\begin{array}{l}\mathrm{CH{-\!-\!-}CO}\\ \mathrm{C(CO_2Et){:}CMe}\end{array}{>}\mathrm{O},$$

is shown by the fact that on esterification it yields a *diethyl* ester, $C_{11}H_{14}O_4$, and a *dimethyl* ester, $C_9H_{10}O_4$, from which the acid may be recovered unchanged on hydrolysis.

It is possible that hydrolysis has taken place with simultaneous loss of carbon dioxide and water with formation of 1-methyl-$\Delta^{1:3}$-*cyclo*butadiene-2 : 4-dicarboxylic acid in accordance with the following scheme:

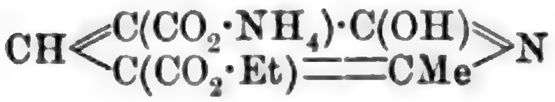


$$\mathrm{CH}{<}\begin{array}{l}\mathrm{C(CO_2Et){-}CO}\\ \mathrm{C(CO_2Et){:}CMe}\end{array}{>}\mathrm{O} \rightarrow \mathrm{CH}{<}\begin{array}{l}\mathrm{C(CO_2H){\cdot}CO_2H}\\ \mathrm{C(CO_2H){:}CMe{\cdot}OH}\end{array} \rightarrow$$

$$\mathrm{CH}{<}\begin{array}{l}\mathrm{CH{\cdot}CO_2H}\\ \mathrm{C(CO_2H){:}CMe{\cdot}OH}\end{array} \rightarrow \mathrm{CH}{<}\begin{array}{l}\mathrm{C(CO_2H)}\\ \mathrm{C(CO_2H)}\end{array}{>}\mathrm{CMe}.$$

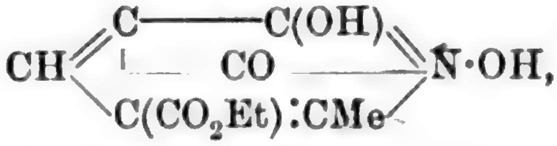
It is hoped that further experiments, which are in progress, will show whether this condensation has taken place.

When ethyl 6-methyl-2-pyrone-3 : 5-dicarboxylate is treated with ammonia, it undergoes an internal change, and is converted into *ethyl ammonium* 6-*hydroxy*-2-*methylpyridine*-3 : 5-*dicarboxylate* (I),



$$\mathrm{CH}{<}\begin{array}{l}\mathrm{C(CO_2{\cdot}NH_4){\cdot}C(OH)}\\ \mathrm{C(CO_2{\cdot}Et){=\!=\!=}CMe}\end{array}{>}\mathrm{N}$$

(I.)



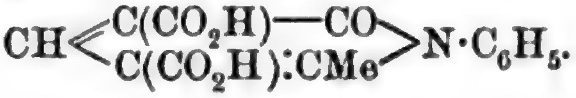
$$\mathrm{CH}\begin{array}{l}\mathrm{C{-\!-\!-}C(OH)}\\ \quad\mathrm{CO}\\ \mathrm{C(CO_2Et){:}CMe}\end{array}\mathrm{N{\cdot}OH},$$

(II.)

and this substance, when treated in the cold with dilute hydrochloric acid, undergoes a curious change, and is converted into a *substance*, which crystallises in sulphur-yellow needles and is insoluble in sodium carbonate. It is probable that this is an internal salt of the formula (II).

The ethyl ammonium salt mentioned above is readily hydrolysed by boiling alcoholic potash, with formation of 6-hydroxy-2-methylpyridine-3 : 5-dicarboxylic acid, which melts at 302° and, when heated at 140—150° with concentrated hydrochloric acid, yields 6-hydroxy-a-picoline.

When ethyl 6-methyl-2-pyrone-3 : 5-dicarboxylate is treated with aniline under the conditions described in the experimental part of this paper (p. 1031), it is converted into the *anilide* of *ethyl a-acetylisoaconitate*, $CO_2Et{\cdot}CHAc{\cdot}CH{:}C(CO_2Et){\cdot}CO{\cdot}NHPh$, which, with boiling alcoholic potash, is converted into 1-*phenyl*-6-*methyl*-*a*-*pyridone*-3 : 5-*dicarboxylic acid*,



$$\mathrm{CH}{<}\begin{array}{l}\mathrm{C(CO_2H){-}CO}\\ \mathrm{C(CO_2H){:}CMe}\end{array}{>}\mathrm{N{\cdot}C_6H_5}.$$

Some of the substances mentioned above, namely, 6-hydroxy-2-methylpyridine-3 : 5-dicarboxylic acid and 6-hydroxy-a-picoline, have already been described by Errera (*Ber.*, 1900, **33**, 2969), who obtained them from the product of the condensation of ethyl ethoxymethyleneacetoacetate and ethyl sodiocyanoacetamide.

Ethyl 6-methyl-2-pyrone-3 : 5-dicarboxylate has been obtained during the course of the present research in four different ways, of which the following may be considered first:

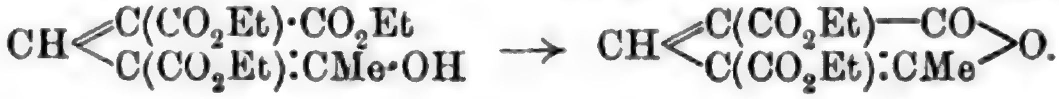
I. Condensation of ethyl ethoxymethylenemalonate and ethyl sodioacetoacetate.

II. Condensation of ethyl ethoxymethyleneacetoacetate and ethyl sodiomalonate.

If it be assumed that ethyl *a*-acetyl*iso*aconitate is the first product of the reaction, then the formation by method I is readily understood:

$$\mathrm{(CO_2Et)_2C{:}CH\cdot OEt + CHNaAc\cdot CO_2Et} \longrightarrow$$

$$\mathrm{(CO_2Et)_2C{:}CH\cdot CHAc\cdot CO_2Et} \longrightarrow$$



$$\mathrm{CH}{<}\begin{matrix}\mathrm{C(CO_2Et)\cdot CO_2Et}\\ \mathrm{C(CO_2Et){:}CMe\cdot OH}\end{matrix} \longrightarrow \mathrm{CH}{<}\begin{matrix}\mathrm{C(CO_2Et)-CO}\\ \mathrm{C(CO_2Et){:}CMe}\end{matrix}{>}\mathrm{O}.$$

But the formation of this ester by method II necessitates a transference of the double linkings:

$$\mathrm{(CO_2Et)_2CHNa + EtO\cdot CH{:}CAc\cdot CO_2Et} \longrightarrow$$

$$\mathrm{(CO_2Et)_2CH\cdot CH{:}CAc\cdot CO_2Et} \longrightarrow$$

$$\mathrm{(CO_2Et)_2C{:}CH\cdot CHAc\cdot CO_2Et.}$$

This curious transference of the double linking in the cases of glutaconic acid and its derivatives has already been observed and discussed by Perkin and Tattersall (Trans., 1905, **87**, 361), and especially by J. F. Thorpe (Trans., 1905, **87**, 1669).

More difficult of explanation is the fact that ethyl 6-methyl-2-pyrone-3 : 5-dicarboxylate is obtained in a quantitative yield from the following condensations:

III. Ethyl ethoxymethyleneacetoacetate and ethyl sodiocyanoacetate.

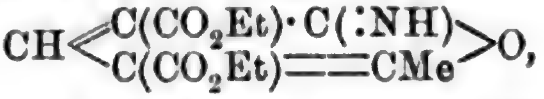
IV. Ethyl ethoxymethylenecyanoacetate and ethyl sodioacetoacetate.

The difficulty in these methods of formation is to explain the way in which the cyanogen groups react. The following, however, seems the most probable explanation. The reaction in the case of IV takes place thus:

$$\mathrm{CO_2Et\cdot C(CN){:}CH\cdot OEt + CHNaAc\cdot CO_2Et} \longrightarrow$$

$$\mathrm{CO_2Et\cdot C(CN){:}CH\cdot CNaAc\cdot CO_2Et.}$$

The sodium compound then undergoes internal condensation with formation of an unstable imino-compound,



$$\mathrm{CH}{<}\begin{matrix}\mathrm{C(CO_2Et)\cdot C(:NH)}\\ \mathrm{C(CO_2Et)=\!=\!=CMe}\end{matrix}{>}\mathrm{O},$$

which reacts with water with loss of ammonia and separation of ethyl 6-methyl-2-pyrone-3:5-dicarboxylate. Since the intermediate product evidently exists in the solution as a sodium derivative, several attempts were made to isolate a methyl derivative by the addition of methyl iodide to its alcoholic solution. On the addition of water, however, no compound separated, and on acidification only the pyrone could be isolated.

EXPERIMENTAL.

The two methods which give the best yields of ethyl 6-methyl-2-pyrone-3:5-dicarboxylate are those mentioned under III and IV in the introduction, and as these are much more convenient than I and II, which give only yields of about 50 per cent., they are described first.

Condensation of Ethyl Ethoxymethyleneacetoacetate and Ethyl Cyanoacetate.

Sodium (2·3 grams) was dissolved in alcohol, and to the well-cooled solution ethyl cyanoacetate (11·3 grams) was added. When the ethyl sodiocyanoacetate had separated, ethyl ethoxymethyleneacetoacetate (18·6 grams) was gradually added, care being taken that no rise in temperature took place.

The sodium derivative immediately dissolved, the solution assuming a pale red colour, and, after standing for two or three minutes, ice was added and the liquid carefully acidified with dilute hydrochloric acid.

On the addition of the first few drops of acid, the red colour rapidly darkened, but on further addition the colour disappeared and a colourless solid consisting of *ethyl* 6-*methyl*-2-*pyrone*-3:5-*dicarboxylate* was precipitated.* This was collected and recrystallised from light petroleum. The yield was quantitative:

0·1207 gave 0·2506 CO_2 and 0·0605 H_2O. C = 56·6; H = 5·6.

$C_{12}H_{14}O_6$ requires C = 56·7; H = 5·5 per cent.

Ethyl 6-*methyl*-2-*pyrone*-3:5-*dicarboxylate* crystallised from light petroleum in long, colourless needles, which melt at 79·5° to a pale red oil. It is readily soluble in most organic solvents, but insoluble in water. With ferric chloride in alcoholic solution, it gives a violet coloration, which deepens considerably on standing. It dissolves readily in concentrated sulphuric acid, and the solution gradually develops a yellowish-green fluorescence.

---

* Ammonium chloride was isolated from the mother liquor on evaporation.

Condensation of Ethyl Ethoxymethylenecyanoacetate and Ethyl Acetoacetate.

The ethyl ethoxycyanoacetate required for these experiments was obtained by the method described by Bollement (*Bull. Soc. chim.*, 1901, [iii], **25**, 20). The melting point was found to be 55°, and not 52—53° as stated by him. The condensation was carried out in a manner analogous to the one just described, and gave a quantitative yield of the pyrone.

0·1154 gave 0·2398 CO_2 and 0·0585 H_2O. C = 56·7; H = 5·6.

$C_{12}H_{14}O_6$ requires C = 56·7; H = 5·5 per cent.

Condensation of Ethyl Ethoxymethyleneacetoacetate and Ethyl Malonate.

In carrying out this condensation, sodium (2·3 grams) was dissolved in alcohol, and to the cold solution a mixture of ethyl malonate (16 grams) and ethyl ethoxymethyleneacetoacetate (18·6 grams) was gradually added, care being taken that no rise in temperature took place. The solution, which became intensely red, was allowed to stand for one hour at the ordinary temperature, ice was added, and the sodium salt decomposed with dilute hydrochloric acid, when a viscid, colourless oil separated. This was dissolved in ether, the ethereal solution well washed with water to remove alcohol, dried, and evaporated. The residual red oil was fractionated in small quantities under diminished pressure (22 mm.), when it distilled at 230—250°. The red distillate solidified completely when cooled in a freezing mixture, and, after pressing on porous porcelain to remove a trace of oily impurity, it was recrystallised from light petroleum:

0·1606 gave 0·3355 CO_2 and 0·0803 H_2O. C = 56·9; H = 5·5.

$C_{12}H_{14}O_6$ requires C = 56·7; H = 5·5 per cent.

The yield was about 50 per cent., but varied somewhat in different preparations.

Condensation of Ethyl Ethoxymethylenemalonate and Ethyl Acetoacetate.

The method adopted in this condensation was analogous to that just described. The yield, however, was not so good, rarely exceeding 40 per cent. A recrystallised specimen gave the following result on analysis:

0·1399 gave 0·2876 CO_2 and 0·0694 H_2O. C = 56·1; H = 5·5.

$C_{12}H_{14}O_6$ requires C = 56·7; H = 5·6 per cent.

Hydrolysis of Ethyl 6-*Methyl*-2-*pyrone*-3:5-*dicarboxylate.*

I. *Hydrolysis with Barium Hydroxide.*—The pyrone (5 grams) was boiled with excess of a concentrated solution of barium hydroxide for an hour, when the ester gradually dissolved with formation of a pale brown solution and separation of much barium carbonate. Excess of barium hydroxide was removed by means of carbon dioxide, the filtered solution concentrated, and, after cooling, acidified with dilute hydrochloric acid, when a pale brown powder separated.

This was collected and recrystallised either from water or a mixture of ether and ethyl acetate with the aid of animal charcoal in each case:

0·1795 gave 0·3571 CO_2 and 0·0640 H_2O. C = 54·0; H = 3·9.

$C_7H_6O_4$ requires C = 54·5; H = 3·9 per cent.

This acid separates from hot water in colourless, microscopic plates. It has no definite melting point, but begins to sinter at 268° and decomposes completely at 300°.

It is readily soluble in hot water, ethyl acetate, or acetic acid, but only sparingly so in benzene or light petroleum even on boiling. With ferric chloride in alcoholic solution it gives no immediate colour, but, on standing, a brown coloration gradually appears, and the solution exhibits a green fluorescence.

When titrated in the cold with *N*/10-sodium hydroxide, it gives numbers agreeing with a dibasic acid of the formula $C_7H_6O_4$.

1·1212 neutralised 0·0632 NaOH, whereas a dibasic acid, $C_7H_6O_4$, should neutralise 0·0629 NaOH.

II. *Hydrolysis with Alcoholic Potassium Hydroxide.*—The ester (10 grams) was boiled with alcoholic potassium hydroxide (10 grams) for an hour, when a deep red solution was formed, from which a pale red potassium salt gradually separated. The whole was dissolved in water, and the brown, fluorescent solution evaporated until free from alcohol and acidified with hydrochloric acid, when a yellowish brown solid (5 grams) was obtained; this was collected and recrystallised from water with the aid of animal charcoal:

0·1308 gave 0·2612 CO_2 and 0·0389 H_2O. C = 54·5; H = 3·3.

$C_7H_6O_4$ requires C = 54·5; H = 3·9 per cent.

This substance was identical with the acid obtained by the hydrolysis with barium hydroxide.

The Methyl Ester of the Acid $C_7H_6O_4$.

In preparing this substance, the acid (3 grams) was boiled with methyl alcohol (30 c.c.) and sulphuric acid (3 c.c.) for two hours, when, on cooling, the methyl ester crystallised out. The ester was dissolved in ether, the ethereal solution was washed with sodium carbonate and water, dried, and, after evaporating the ether, the residue was purified by crystallisation from light petroleum:

0·1306 gave 0·2827 CO_2 and 0·0656 H_2O. $C = 59·0$; $H = 5·6$.
0·1415 „ 0·3098 CO_2 „ 0·0679 H_2O. $C = 59·6$; $H = 5·3$.
$C_9H_{10}O_4$ requires $C = 59·3$; $H = 5·4$ per cent.

This *methyl* ester separates from light petroleum or methyl alcohol in colourless, long, silky needles, which melt at 106°. Its alcoholic solution gives no colour with ferric chloride.

The Ethyl Ester, $C_{11}H_{14}O_4$.

The ethyl ester of the acid $C_7H_6O_4$ was prepared in a manner similar to the above. It crystallised from light petroleum in clusters of colourless needles melting at 48°:

0·1179 gave 0·2693 CO_2 and 0·0652 H_2O. $C = 62·2$; $H = 6·2$.
$C_{11}H_{14}O_4$ requires $C = 62·8$; $H = 6·7$ per cent.

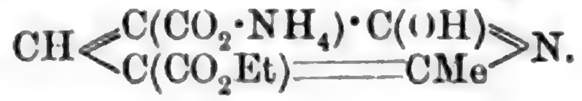
Hydrolysis of the Methyl Ester.—In order to be certain that no change had taken place during the esterification, the methyl ester (2 grams) was boiled with 25 c.c. of 25 per cent. hydrochloric acid for three hours. After cooling, the solution was saturated with ammonium sulphate, and the acid which separated was extracted with ether. After removal of the ether, the acid was crystallised from water and dried at 110°.

0·1209 gave 0·2415 CO_2 and 0·0461 H_2O. $C = 54·4$; $H = 4·2$.
$C_7H_6O_4$ requires $C = 54·5$; $H = 3·9$ per cent.

That the acid was identical with that obtained by the barium hydroxide hydrolysis described above was shown by the decomposition point (300°), and by the following titration:

0·0875 neutralised 0·046 NaOH, whereas a dibasic acid, $C_7H_6O_4$, should neutralise 0·046 NaOH.

Action of Ammonia on Ethyl 6-Methyl-2-pyrone-3:5-dicarboxylate. Formation of Ethyl Ammonium 6-Hydroxy-2-methylpyridine-3:5-dicarboxylate,



$$CH<\begin{matrix}C(CO_2\cdot NH_4)\cdot C(OH)\\ C(CO_2Et)=\!=\!=\!=CMe\end{matrix}>N.$$

When ethyl 6-methyl-2-pyrone-3:5-dicarboxylate (3 grams) is ground up with water (5 c.c.) and mixed with strong ammonia (5 c.c.), much heat is generated, and the colourless 2-pyrone is converted into a pink solid. This was collected, washed with a little water, and drained on porous porcelain, when 3 grams of the ammonium salt were obtained; this was crystallised from dilute alcohol and dried at 100°:

0·1145 gave 0·2081 CO_2 and 0·0589 H_2O. $C = 49·5$; $H = 5·7$.
0·1889 „ 17·8 c.c. of nitrogen at 15° and 770 mm. $N = 11·2$.
$C_{10}H_{14}O_5N_2$ requires $C = 49·6$; $H = 5·8$; $N = 11·5$ per cent.

This substance, which evidently consisted of *ethyl ammonium 6-hydroxy-2-methylpyridine*-3 : 5-*dicarboxylate*, in which it is assumed that the carboxyl group in the position 5 has been hydrolysed, melted at 263—265° with decomposition.

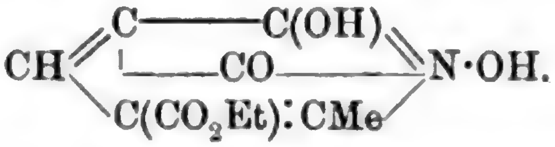
It is sparingly soluble in most organic solvents, but separates from water or dilute alcohol as a pale yellow powder, which, under the microscope, was seen to consist of stellate clusters of needles. Its alcoholic solution exhibits a characteristic blue fluorescence, but gives no colour with ferric chloride.

Its aqueous solution gives with silver nitrate solution a voluminous precipitate of the *silver* salt :

0·2014 gave 0·0655 Ag. $Ag = 32·5$.
$C_{10}H_{10}O_5NAg$ requires $Ag = 32·5$ per cent.

Action of Hydrochloric Acid on Ethyl Ammonium 6-Hydroxy-2-methylpyridine-3 : 5-*dicarboxylate.*

Attention has already been drawn to the fact in the introduction that, when ethyl ammonium 6-hydroxy-2-methylpyridine-3 : 5-dicarboxylate is treated with hydrochloric acid, it undergoes a strange decomposition, and is converted into a substance to which the following formula may possibly be ascribed :



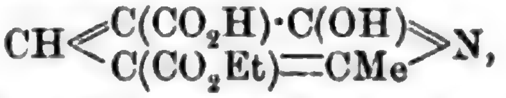
$$\mathrm{CH}\left\langle\begin{array}{l}\mathrm{C}\text{———}\mathrm{C(OH)}\\ \mid\text{———}\mathrm{CO}\text{———}\\ \mathrm{C(CO_2Et){:}CMe}\end{array}\right\rangle\mathrm{N{\cdot}OH}.$$

The ammonium salt (2 grams) was mixed with water (5 c.c.), a few c.c. of dilute hydrochloric acid were added, and the pasty mass was triturated in a mortar. After standing for about ten minutes, the pale yellow powder was collected, crystallised from alcohol with the aid of animal charcoal, and dried at 110° :

0·1311 gave 0·2574 CO_2 and 0·0607 H_2O. $C = 53·5$; $H = 5·1$.
0·1717 „ 9·1 c.c. of nitrogen at 12° and 770 mm. $N = 6·4$.
$C_{10}H_{11}O_5N$ requires $C = 53·3$; $H = 4·9$; $N = 6·2$ per cent.

The substance melts at 223° and is insoluble in water, but readily soluble in hot alcohol, from which it separates in beautiful sulphur-yellow, prismatic needles. It dissolves only sparingly in ether, light petroleum, or ethyl acetate even on boiling. Its alcoholic solution shows a characteristic blue fluorescence, but gives no colour with ferric chloride.

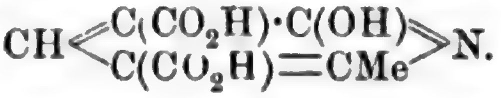
That this substance is not the acid ester,



$$\mathrm{CH}{<}\begin{matrix}\mathrm{C(CO_2H)\cdot C(OH)}\\ \mathrm{C(CO_2Et){=}CMe}\end{matrix}{>}\mathrm{N},$$

is shown by the fact that it is quite insoluble in cold dilute sodium carbonate solution, and even on boiling it dissolves only sparingly; it is, however, readily soluble in dilute aqueous potassium hydroxide. Concentrated ammonia immediately reconverts it into the ammonium salt from which it was obtained. When hydrolysed with alcoholic potash, it is converted into 6-hydroxy-2-methylpyridine-3 : 5-dicarboxylic acid.

6-Hydroxy-2-methylpyridine-3 : 5-dicarboxylic Acid,



$$\mathrm{CH}{<}\begin{matrix}\mathrm{C(CO_2H)\cdot C(OH)}\\ \mathrm{C(CO_2H){=}CMe}\end{matrix}{>}\mathrm{N}.$$

This acid, which has already been described by Errera (*loc. cit.*), is best obtained when ethyl ammonium 6-hydroxy-2-methylpyridine-3 : 5-dicarboxylate is boiled with excess of alcoholic potash until no further evolution of ammonia can be detected.

After freeing the solution from alcohol by evaporation and acidifying, the free acid separated as a pale yellow, crystalline powder, which, after crystallising from hot water with the aid of animal charcoal, was obtained in colourless, prismatic, needles containing, when dried at 100°, half a molecule of water of crystallisation:

0·1273 gave 0·2182 CO_2 and 0·0479 H_2O. C = 46·7; H = 4·2.
0·1346 „ 8·1 c.c. of nitrogen at 15° and 740 mm. N = 6·9.
$C_8H_7O_5N,\frac{1}{2}H_2O$ requires C = 46·6; H = 3·9; N = 6·8 per cent.

When dried at 115°, the anhydrous acid was obtained:

0·1423 gave 0·2558 CO_2 and 0·0447 H_2O. C = 49·1; H = 3·5.
$C_8H_7O_5N$ requires C = 48·7; H = 3·5 per cent.

6-Hydroxy-2-methylpyridine-3 : 5-dicarboxylic acid has a decomposition point which varies considerably with the method of heating; when fairly rapidly heated, it decomposes quite sharply at 302° (Errera gives 303°).

It is readily soluble in hot water or alcohol, but only sparingly so in ether, benzene, acetic acid, or ethyl acetate, and its solution gives no colour with ferric chloride.

Contrary to the statement of Errera (*loc. cit.*, p. 2971), 6-hydroxy-2-methylpyridine-3 : 5-dicarboxylic acid exhibits a great tendency to form well-characterised crystalline salts.

A faintly alkaline solution of its ammonium salt gives with barium chloride an immediate gelatinous precipitate, which on boiling crystallises and, under the microscope, is seen to consist of beautiful clusters of needles. The *copper* salt is also highly characteristic, and crystallises in masses of striated plates. The acid also readily forms insoluble *silver* and *calcium* salts. The *barium* salt was selected for analysis. After drying at 115° until constant, it gave the following result:

0·3107 gave 0·1974 $BaSO_4$. $Ba = 37·4$.

$C_8H_5O_5NBa,2H_2O$ requires $Ba = 37·2$ per cent.

6-*Hydroxy-a-picoline.*

As has been stated by Errera (*loc. cit.*, 2971), this substance is readily obtained from 6-hydroxy-2-methylpyridine-3:5-dicarboxylic acid by heating in a sealed tube with concentrated hydrochloric acid for about one hour at 140—150°. The clear solution is evaporated to dryness, and the residual crude hydrochloride crystallises from a mixture of chloroform and alcohol, when it is readily obtained pure in colourless plates containing one molecule of water of crystallisation, which is not removed in a vacuum over sulphuric acid:

0·1284 gave 0·1121 AgCl. $Cl = 21·6$.

C_6H_8OCl,H_2O requires $Cl = 21·7$ per cent.

6-Hydroxy-a-picoline hydrochloride melts at 117—118°, and could not be obtained in a pure anhydrous condition, since when dried at 100° it slowly loses hydrogen chloride.

6-Hydroxy-a-picoline is readily obtained when an aqueous solution of the hydrochloride is neutralised with sodium carbonate. On the addition of ammonium sulphate, the base separates in long, silky needles containing water of crystallisation. After drying at 100° and recrystallising from benzene, it melted at 159°:

0·1503 gave 0·3624 CO_2 and 0·0859 H_2O. $C = 65·8$; $H = 6·3$.

C_6H_7ON requires $C = 66·1$; $H = 6·4$ per cent.

Action of Aniline on Ethyl 6-Methyl-2-pyrone-3:5-dicarboxylate. Formation of the Anilide of Ethyl a-Acetylisoaconitate,

$CO_2Et·CHAc·CH:C(CO_2Et)·CO·NHPh$.

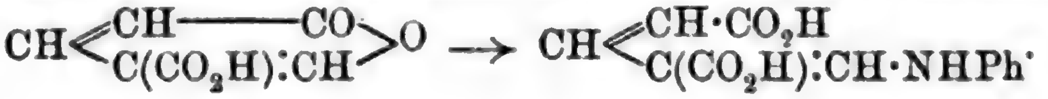
Ethyl 6-methyl-2-pyrone-3:5-dicarboxylate (5 grams) was dissolved in aniline (4 grams) and heated for three hours on the water-bath. After cooling, alcohol was added, when a colourless, crystalline solid separated. This was collected and recrystallised from alcohol, from which it separated in lustrous, thin plates resembling acetanilide, which melt at 188°:

0·1357 gave 0·3114 CO_2 and 0·0752 H_2O. $C = 62·6$; $H = 6·1$.

$C_{18}H_{21}O_6N$ requires $C = 62·3$; $H = 6·0$ per cent.

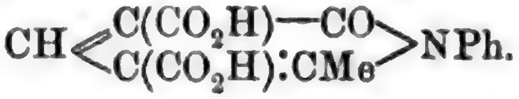
The *anilide* of *ethyl a-acetylisoaconitate* is readily soluble in chloroform, acetone, ethyl acetate, or hot alcohol, but only sparingly so in benzene or ether. Its alcoholic solution gives with ferric chloride a deep brown coloration.

Since it is insoluble in sodium carbonate, it cannot have the constitution $\mathrm{NHPh{\cdot}CMe{:}C(CO_2Et){\cdot}CH{:}C(CO_2Et){\cdot}CO_2H}$, which would be analogous to the substance obtained by von Pechmann and Welsh (*Ber.*, 1884, **17**, 2393) by the action of aniline on ethyl coumalinate:



$$\mathrm{CH}{<}\begin{matrix}\mathrm{CH}\text{———}\mathrm{CO}\\ \mathrm{C(CO_2H){:}CH}\end{matrix}{>}\mathrm{O} \longrightarrow \mathrm{CH}{<}\begin{matrix}\mathrm{CH{\cdot}CO_2H}\\ \mathrm{C(CO_2H){:}CH{\cdot}NHPh}\end{matrix}$$

1-*Phenyl*-6-*methyl*-2-*pyridone*-3 : 5-*dicarboxylic Acid*,



$$\mathrm{CH}{<}\begin{matrix}\mathrm{C(CO_2H)}\text{—}\mathrm{CO}\\ \mathrm{C(CO_2H){:}CMe}\end{matrix}{>}\mathrm{NPh.}$$

This acid was prepared by boiling the anilide of ethyl a-acetyl*iso*aconitate with excess of alcoholic potash for a short time. After removing the alcohol and acidifying, the acid was obtained as a pale yellow solid, which was crystallised from dilute alcohol with the aid of animal charcoal:

0·1191 gave 0·2675 CO_2 and 0·0478 H_2O. C = 61·2 ; H = 4·4.

$C_{14}H_{11}O_5N$ requires C = 61·5 ; H = 4·0 per cent.

1-*Phenyl*-6-*methyl*-2-*pyridone*-3 : 5-*dicarboxylic acid* separates from alcohol in colourless, feathery needles, which melt with decomposition at 265—267°. It is readily soluble in hot alcohol, benzene, or ethyl acetate, but only sparingly so in water or ether. Its solution gives no colour with ferric chloride.

On the addition of silver nitrate to a faintly alkaline solution of its ammonium salt, the *silver* salt is obtained as a microcrystalline powder:

0·1010 gave 0·0499 Ag. Ag = 44·4.

$C_{14}H_9O_5NAg_2$ requires Ag = 44·3 per cent.

The author wishes to thank the Research Fund Committee of the Chemical Society for a grant which has defrayed much of the expense of this research.

THE SCHUNCK LABORATORY,
THE UNIVERSITY, MANCHESTER.

CI.—*The Melting Points of the Anilides*, p-*Toluidides, and α-Naphthalides of the Normal Fatty Acids.*

By PHILIP WILFRED ROBERTSON.

UNTIL von Baeyer showed that the melting points of the normal fatty acids alternately rose and fell with each successive addition of a carbon atom to the hydrocarbon chain, and that a regular series of numbers could be obtained only by considering the odd or even members separately, it had generally been recognised that the melting points of an homologous series increased regularly with the number of carbon atoms in the molecule. Owing to lack of data, a similar relationship has been established only in a very few cases; as examples may be cited the dibasic acids of the oxalic series and the substituted malonic acids. In both these cases, in order to obtain a regular series of melting points, it is necessary separately to consider the odd and even members, and then the general result is a fall to a minimum followed by a gradual rise. Very complete data are also available for another series, namely, the amides of the fatty acids (table I). But here the utmost irregularity appears to prevail even when a separate comparison is made among the odd or even members. As the available data for the corresponding anilides showed traces of a similar irregularity, it was decided to complete the series as far as possible and to prepare the missing compounds. Then, finally, to throw more light on the whole problem and to endeavour to obtain a more definite insight into the relationships between the melting point and the number of carbon atoms in such homologous series, the *p*-toluidides and α-naphthalides of the normal fatty acids were also prepared.

TABLE I.

Number of carbon atoms in acid.	Amides. M.p.	Anilides. M.p.	*p*-Toluidides. M.p.
2	82°	112°	153°
3	79*	105*	123°
4	115	92	74*
5	115	61	72*
6	100	95	75*
7	95	71	80*
8	110	57*	67*
9	92	57*	81*
10	98	61*	80*
11	81	64*	73*
12	112	68*	81*
14	102	84	93*
16	101	90	96*
18	109	94	98*

* Determinations by the author.

A consideration of the above series shows that there is a tendency to regularity in the irregularity itself. Thus, among the even members of the anilides and *p*-toluidides, it is seen that there is a considerable fall from the second to the fourth member, followed by a slight rise and then another fall, and that after the eighth member the melting points continue to rise, although in both series the derivative of the twelfth acid has a melting point considerably lower than might be expected from its position in the series. If, now, attention is directed to the amides, it is observed that the irregularity tends in the reverse direction. There is a considerable rise from the second to the fourth member, followed by a fall, and then again another rise and again a fall to the tenth member, each change being exactly in the reverse direction to that observed among either the anilides or *p*-toluidides; further, the C_{12} amide has a higher melting point than the contiguous members, whereas it was noticed that the melting points of the corresponding anilide and *p*-toluidide appeared abnormally low. Also among the odd members the same general tendencies are observable, there being a rise followed by a fall in the case of the first three uneven amides, whilst the reverse is true for the other two series.

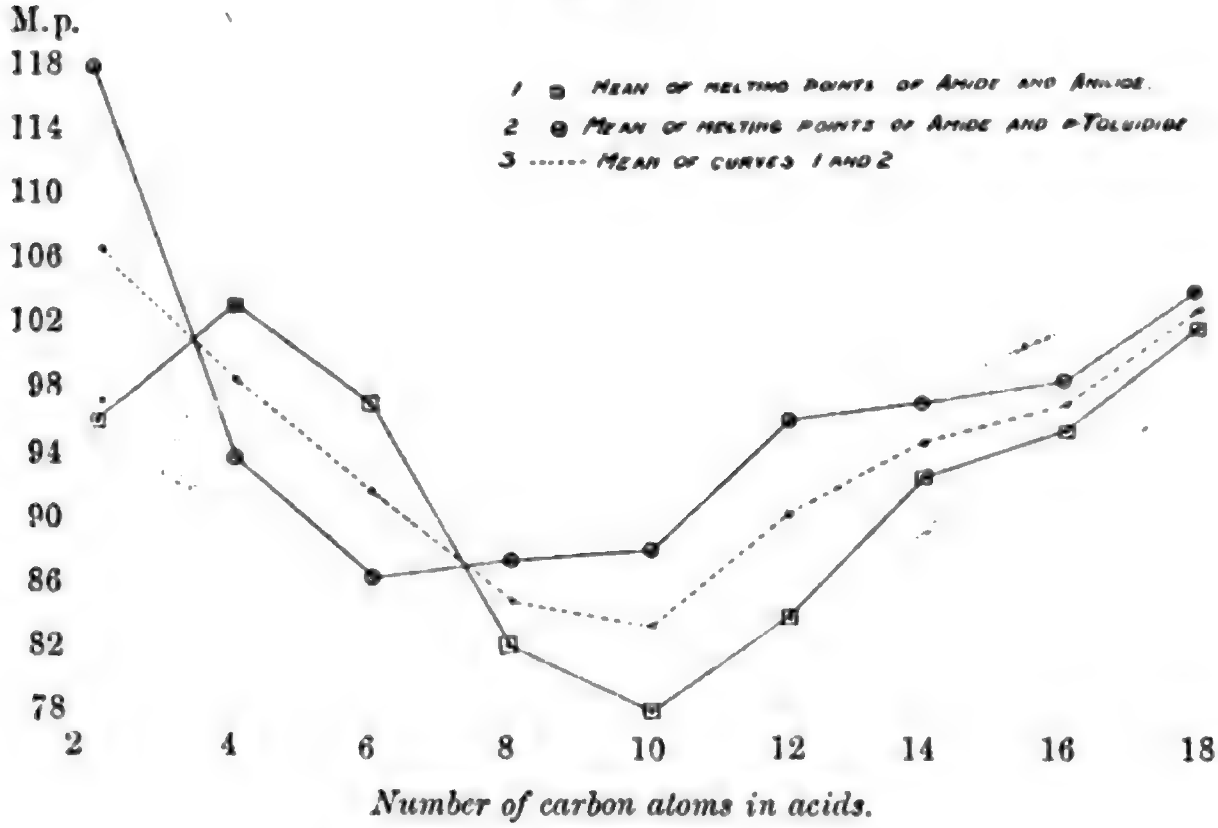
Considerations of this nature seem clearly to indicate that there is some definite factor exerting an influence in the one case tending to lower the melting points, and in the other case having the reverse effect. The exact nature of this disturbing influence is difficult to realise, but the suggestion is tentatively ventured that it is some function of the symmetry or rather lack of symmetry of the molecule. There appears no doubt that molecular symmetry has not an inconsiderable influence on the melting point, as has been definitely established from the investigation of isomeric compounds, it being almost universally observed that the most symmetrical isomeride has the highest melting point. It appears then to be a legitimate assumption to make that if the arithmetical mean of the melting points of the amides and anilides and of the amides and *p*-toluidides was taken, then this disturbing factor might be to some extent eliminated and two regular series should be expected. This is actually found to be the case (table II).

The numbers for the odd members decrease regularly as far as the data are available. The results for the even members are plotted in Fig. 1. The curve for the amides and *p*-toluidides reaches a minimum at the sixth member and then rises gradually, and the corresponding curve for the amides and anilides shows a minimum at the tenth member and a maximum at the fourth. The occurrence of this maximum can scarcely be considered as an irregularity, as it has been previously observed that a maximum and minimum occur in the same series at a difference of six carbon atoms (compare the molecular

TABLE II.—*Mean of Melting Points.*

Number of carbon atoms in acid.	Amide and anilide.	Amide and p-toluidide.
2	97°	117·5°
3	92°	101°
4	103·5	94·5
5	88	93·5
6	97·5	87·5
7	83	87·5
8	83·5	88·5
9	74·5	86·5
10	79·5	89
11	72·5	77
12	85	96·5
14	93	97·5
16	95·5	98·5
18	101·5	103·5

FIG. 1.



depressions of the fatty esters in phenol solution, Trans., 1905, **87**, 1581), a result which can possibly be correlated with the fact that a chain of six carbon atoms bends round on itself in space. On taking the mean of the two curves (Fig. 1), further influences of the disturbing factor, whether it be lack of symmetry or some other cause, appear to be eliminated, and the resultant dotted curve is quite regular. It can scarcely be imagined that the regularity and symmetry of this dotted curve is altogether accidental, and it may be considered as a typical melting-point curve for compounds of the general formula $CH_3\cdot[CH_2]_n\cdot CO\cdot NHX$, after the disturbing influences of alterations in symmetry have been eliminated.

Finally, a series was investigated, namely, the fatty α-naphthylalides (table III), in which the grouping X was heavier. The same alteration between the odd and even members persists, but the other irregularities have disappeared; the compounds with an even number of carbon atoms form a regular series with a minimum at the eighth member, and there is a similar odd series falling to a minimum at the ninth member.

TABLE III.

Number of carbon atoms in acid.	Melting points of α-naphthalides.		Number of carbon atoms in acid.	Melting points of α-naphthalides.	
2	202°		9		91*
3		116°*	10	99*	
4	120*		11		92*
5		111*	12	100*	
6	112*		14	105*	
7		106*	16	106*	
8	95*		18	110*	

* Determinations by the author.

EXPERIMENTAL.

The anilides, *p*-toluidides, and α-naphthalides described in the present paper were prepared by the following method. A mixture of 1 to 3 grams of the fatty acid and the equivalent amount of amine was heated in a sealed tube to 160—190° for eight to twelve hours. In no case was any pressure observed in the tube after cooling. The product of the reaction, generally a solid or an oil which soon solidified, was purified by recrystallisation from aqueous alcohol, or, in the case of the derivatives of the higher fatty acids, absolute alcohol. In certain cases, when the product tended to be oily, it was found advisable first to spread the mass on a porous tile and leave for twenty-four hours before recrystallisation. The yields varied between 30 and 80 per cent., depending largely on the degree of purity of the fatty acid employed. The anilides and *p*-toluidides were pure white or faintly yellow; the α-naphthalides generally had a pink colour, not unlike that which α-naphthylamine acquires on contact with the air. On boiling in alcoholic solution with animal charcoal, all traces of pink colour could be removed without, however, affecting the melting point. When pure, the α-naphthalides were completely free from the objectionable odour of the base.

On page 1037 are the new compounds described, with the results of the analyses:

TABLE IV.

Compound.	Formula.	M. p.	Percentage of nitrogen found.	Percentage of nitrogen theory.
n-Octanilide	$C_{14}H_{21}ON$	57°	6·4	6·4
n-Nonanilide	$C_{15}H_{23}ON$	57	6·3	6·0
n-Decanilide	$C_{16}H_{25}ON$	61	5·9	5·7
n-Undecanilide	$C_{17}H_{27}ON$	64	5·6	5·3
Lauranilide	$C_{18}H_{29}ON$	68	5·1	5·0
n-Butyro-*p*-toluidide	$C_{11}H_{15}ON$	74	8·0	7·8
n-Valero-*p*-toluidide	$C_{12}H_{17}ON$	72	7·5	7·3
n-Hexo-*p*-toluidide	$C_{13}H_{19}ON$	75	7·0	6·8
n-Hepto-*p*-toluidide	$C_{14}H_{21}ON$	80	6·3	6·4
n-Octo-*p*-toluidide	$C_{15}H_{23}ON$	67	6·2	6·0
n-Nono-*p*-toluidide	$C_{16}H_{25}ON$	81	5·7	5·7
n-Deco-*p*-toluidide	$C_{17}H_{27}ON$	80	5·5	5·3
n-Undeco-*p*-toluidide	$C_{18}H_{29}ON$	67	5·0	5·0
Lauro-*p*-toluidide	$C_{19}H_{31}ON$	81	5·0	4·8
Myristo-*p*-toluidide	$C_{21}H_{35}ON$	93	4·3	4·4
Palmito-*p*-toluidide	$C_{23}H_{39}ON$	96	4·1	4·0
Stearo-*p*-toluidide	$C_{25}H_{43}ON$	98	3·9	3·8
Propio-*α*-naphthalide	$C_{13}H_{13}ON$	116	7·0	7·0
n-Butyro-*α*-naphthalide	$C_{14}H_{15}ON$	120	6·8	6·6
n-Valero-*α*-naphthalide	$C_{15}H_{17}ON$	111	6·5	6·2
n-Hexo-*α*-naphthalide	$C_{16}H_{19}ON$	112	6·0	5·8
Hepto-*α*-naphthalide	$C_{17}H_{21}ON$	106	5·5	5·5
Octo-*α*-naphthalide	$C_{18}H_{23}ON$	95	5·5	5·2
Nono-*α*-naphthalide	$C_{19}H_{25}ON$	91	5·1	5·0
Deco-*α*-naphthalide	$C_{20}H_{27}ON$	99	5·0	4·8
Undeco-*α*-naphthalide	$C_{21}H_{29}ON$	92	4·9	4·6
Lauro-*α*-naphthalide	$C_{22}H_{31}ON$	100	4·1	4·4
Myristo-*α*-naphthalide	$C_{24}H_{35}ON$	105	3·9	4·0
Palmito-*α*-naphthalide	$C_{26}H_{39}ON$	106	3·8	3·7
Stearo-*α*-naphthalide	$C_{28}H_{43}ON$	110	3·6	3·4

The above research was begun some years ago in New Zealand under the direction of Prof. Easterfield, to whom my best thanks are due for his kind interest and helpful advice, and finished in Oxford.

TRINITY COLLEGE,
OXFORD.

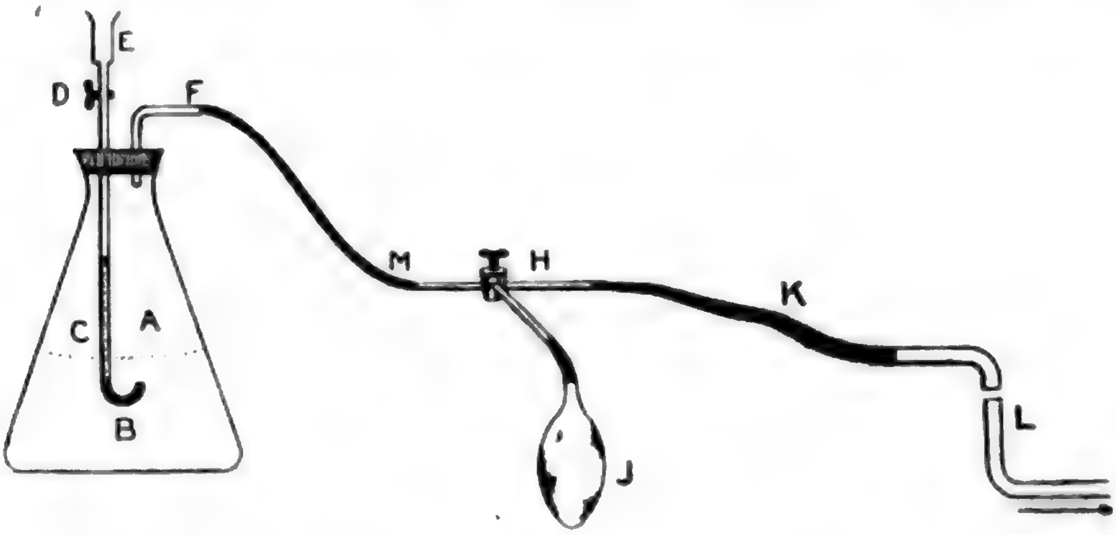
CII.—*The Volumetric Estimation of Silver.*

By WILLIAM ROBERT LANG and JOHN OBINS WOODHOUSE.

IN this journal (Lang and Allen, Trans., 1907, **91**, 1370) there was described an apparatus for the estimation of sulphates and salts of barium based on the rapid clearing of turbid solutions in narrow tubes. The same apparatus was used to determine silver by standard sodium chloride with a view to improving on the well-known Gay-Lussac method, but great difficulty was experienced in determining the end-point, the silver solutions not clearing sufficiently rapidly. The apparatus was therefore modified considerably, with the result that estimations of silver were done in half an hour with an average error of less than a-tenth of one per cent.

The principal differences from the former apparatus were the use of fine sand to retain the silver chloride precipitate, the replacement of the funnel by a short piece of thin-walled glass tubing, which enables the slightest opalescence to be easily observed, and the permanent attachment to an exhaust for washing the precipitate and solution down the tube.

A rubber cork, pierced with two holes, is inserted in a flask, *A*, of about 600 c.c. capacity. Through it passes a tube, *C*, of about 60 mm. diameter, fitted with a stopcock, *D*, and to its upper end is sealed about 4 cm. of a thin test-tube, *E*, of 1—1·5 cm. diameter. About 8 cm. from the lower end of the tube *C*, a plug of glass-wool is inserted and the remainder filled with sand, previously washed free from impurities. The sand is held in its place by a second plug of glass-wool, and the curved piece of tubing, *B*, filled with glass-wool and attached to *C* by a small piece of rubber tubing. The curved portion may, of course, be sealed on, but in these circumstances is not so readily filled. This prevents the back suction from displacing the sand. Through the second hole in the cork a small piece of tubing passes, connected by a length of rubber tubing, *F.M*, to a three-way tap, *H*. *J* is a small hand aspirator to force a portion of the contents of *A* up the tube *C* for titration in *E*, whilst *K* leads to the exhaust pump. It is advisable to have a space between the tap *H* and the water pump, as this ensures there always being a ready vacuum available the moment the connexion is made through *H* to the flask.



The first set of experiments was made with quantities of a solution of silver nitrate of known strength, using *N*/10 sodium chloride in excess as precipitant, and titrating back with *N*/10 silver nitrate. A portion of the silver solution, equivalent to 0·5 gram of silver, is placed in the flask *A* and diluted to about 100 c.c. with distilled water, 50 c.c. of the *N*/10 sodium chloride solution is then run into the flask directly, and the whole heated to boiling to coagulate the precipitated silver chloride.

N/10 Silver nitrate is then run in directly to the solution and precipitate up to within a few c.c. of the calculated amount necessary. The rubber cork with its attachment is replaced and the three-way tap, *H*, opened, and air drawn through the solution for a few minutes. This materially assists the settling of the precipitate. The tap is adjusted, and by means of the aspirator, *J*, some of the liquid and precipitate forced through the layer of sand and glass-wool * into *E*, which it reaches in a perfectly clear condition, the silver chloride being completely retained by the sand. A drop of *N*/10 silver nitrate is added, when a precipitate is formed, varying in intensity with the excess of salt still present. The liquid and precipitate are then sucked and washed down into *A*, and, if the thickness of the precipitate justifies it, about 1 c.c. of the silver solution is added *directly* to the contents of the flask. The stopper is again inserted, and the operation of forcing the mixture up into *E*, titrating, and washing down again, continued until no change is visible in the clear liquid, when a drop of the silver solution is added. The thin walls of *E* render the faintest opalescence readily observable, more particularly if a corresponding glass tube containing distilled water be used for comparison. The results of the first set of experiments are as follows:

In each case, 50 c.c. of silver nitrate solution were employed (= 0·5 gram Ag) and 50 c.c. of a solution of sodium chloride added, each c.c. of which is equivalent to 0·01081 gram Ag. This corresponds with 50·0463 c.c. *N*/10 sodium chloride. On titrating back and calculating the amount of silver equivalent to the nett sodium chloride used by the sample, the errors varied from zero to + 0·54 per cent. Each titration required twenty minutes.

In order to reduce this error, if possible, samples containing 1 gram of silver were taken, 100 c.c. of sodium chloride added (1 c.c. = 0·01081 gram Ag), and the excess titrated back with *N*/100 silver nitrate solution (table I).

As in analyses of silver alloys by Gay-Lussac's method, the precipitation is effected in the presence of free nitric acid, a series of experiments was carried out to ascertain the effect of varying proportions of acid. The volume of the solution containing 1 gram of silver was 100 c.c.; the amount of acid varied from 10 c.c. to 50 c.c., and the resulting errors from + 0·094 to − 0·216 per cent., the mean error being − 0·0634 per cent., the presence of the nitric acid thus tending to make the precipitation more complete.

---

* Glass-wool and asbestos were found to be incapable of retaining the precipitate.

TABLE I.

Grams Ag employed.	*N*/100-AgNO$_3$ used to titrate back, in c.c.	Nett *N*/10-NaCl used, in c.c.	Equiv. to grams Ag.	Diff. in Ag found, in grams.	Error per cent.
1·0	72·00	92·8926	1·0032	0·0032	+0·32
1·0	76·20	92·4726	0·9987	0·0013	−0·13
1·0	75·05	92·5876	0·99994	0·00006	−0·006
1·0	73·20	92·7726	1·0019	0·0019	+0·19
1·0	72·30	92·8626	1·0029	0·0029	+0·29

Average error = +0·266 per cent. and 0·068 per cent. Mean error = 0·198 per cent.
Average time taken = 27 minutes.

To test the usefulness of this apparatus as applied to the practical estimation of silver in bullion, the usual conditions under which this is done by the Gay-Lussac method were adhered to, namely, 1 gram of pure silver dissolved in about 15 c.c. of nitric acid, 100 c.c. of *N*/10 sodium chloride added, and the excess titrated with *N*/100 silver nitrate. (When necessary, any excess of silver solution added was titrated with *N*/100 sodium chloride.)

The following table contains the results of these experiments, and the time taken:

TABLE II.

Grams Ag employed.	*N*/100-AgNO$_3$ used to titrate back, in c.c.	Nett *N*/10-NaCl used, in c.c.	Equiv. to grams Ag.	Diff. in Ag found, in grams.	Error per cent.
1·004	72·00	92·8926	1·0032	0·0008	−0·08
1·000	73·30	92·7626	1·0018	0·0018	+0·18
0·9994	74·75	92·6176	1·00027	0·00087	+0·087
1·0018	73·80	92·7126	1·00129	0·0005	−0·05
1·0034	73·00	92·7926	1·0021	0·0013	−0·13
1·0030	72·30	92·8626	1·0029	0·0001	−0·01
1·0035	72·30	92·8626	1·0029	0·0006	−0·06

Average error = −0·066 per cent. and +0·133 per cent.
Mean error = −0·067 per cent. Average time taken = 30 minutes.

It may be added that no excessive shaking up of the mixture is required other than sufficient to ensure proper mixing after each addition of the reagent.

CHEMICAL LABORATORY,
UNIVERSITY OF TORONTO.

CIII.—*The Polarimetric Study of Intramolecular Rearrangement in Inactive Substances.*

By Thomas Stewart Patterson and Andrew McMillan,
M.A., B.Sc. (Carnegie Research Scholar).

In two recent papers (Trans., 1907, **91**, 504; *Ber.*, 1907, **40**, 2564), we have shown that when certain inactive compounds capable of undergoing intramolecular rearrangement are dissolved in active liquids, it is possible to follow the change of constitution of the inactive substance by observing a corresponding alteration in the rotation of the active solvent. We showed that the *syn*-form of benzaldoxime and of anisaldoxime has a much more pronounced effect on the rotation of ethyl tartrate than has the corresponding *anti*-oxime, so that in a solution containing only one or two per cent. of optically inactive substance, the velocity of rearrangement can easily be observed and can be measured with fair accuracy.

This behaviour seems to apply to aromatic aldoximes generally, the two forms of which have different solvent influences, not only on ethyl tartrate, but also on methyl- and *n*-propyl-tartrate and methyl-, ethyl-, and *n*-propyl-malate. That the process is not confined only to oximes was proved by an experiment with ethyl formylphenylacetate, in which the change from the enol-form to the aldo-form could be traced by observing the gradual increase in the rotation of ethyl tartrate in which the substance was dissolved.

The present paper gives an account of some further experiments which we have carried out on this subject with a view partly to extend the scope of the method to include other types of intramolecular change, partly to ascertain more definitely the most favourable procedure, and partly to obtain greater accuracy in the numerical results. The last of these desiderata has been rendered possible by the generosity of the Carnegie Trustees for the Universities of Scotland, who have placed at the disposal of one of us an excellent Schmidt and Haensch polarimeter together with a thermostat of his own design for use with it.

The thermostat is a large copper bath, about 50 litres capacity, through which passes a copper tube wide enough to contain the polarimeter tubes. This tube is closed at each end by glass disks, and the whole apparatus is so arranged that the axes of the instrument and the polarimeter tube lying in the thermostat coincide. The water in the thermostat is well stirred, and the temperature is kept constant by means of a thermo-regulator designed by one of us (*J. Soc. Chem. Ind.*, 1902, **21**, 456). This regulator has two bulbs, and is filled with about 80 c.c. of benzene. Its accuracy leaves little to be desired; the bath can very easily be brought to any desired temperature (within reasonable limits), and can be kept within 0·01° of that temperature for weeks at a time without the slightest trouble.

As our own former experiments seemed to show that the purity of the active substance used is of importance in determining the velocity of transformation of a labile substance dissolved in it, we first investigated the effect of repeated distillation of the ethyl tartrate. As it may be of some importance for later reference, we give an outline of our preparation of the ester. A mixture of tartaric acid with about twice its weight of alcohol was saturated with hydrogen chloride. The excess of alcohol was then distilled off under diminished pressure (using a water-bath), the original quantity of alcohol added, and the saturation and distillation repeated. The ethyl tartrate was then distilled under reduced pressure, without separation into fractions, and the product was redistilled, a first fraction being rejected. We shall refer to ethyl tartrate prepared in this way as "twice distilled," but, of course, it is obvious that this is only a very rough way of indicating the purity of the ester, which would depend on the size of the rejected fraction.

As a suitable labile compound, we have used mostly piperonal*syn*-oxime. It was prepared by passing dry hydrogen chloride into a flask containing the *anti*-oxime dissolved in ether (not by bubbling the gas through the liquid), and then decomposing the precipitated hydrochloride by excess of sodium carbonate solution. The impure *syn*-oxime, after drying on a porous plate, was subjected anew to the whole process, and the resulting product crystallised from methyl alcohol. For each experiment, it was recrystallised a few hours before the solution was made up; M. p. 146°.

A solution containing 4·98 per cent.* of this *syn*-oxime in the ethyl tartrate "twice distilled" was then examined in the polarimeter from time to time with the following results. (T = time in minutes from the preparation of the solution, a = total change in rotation between T_0 and T_∞, k is calculated from the equation: $k = \frac{1}{T}\log_e\frac{a}{a-x}$, where x is the change in rotation after time T.)

---

* In the tables, the concentration is expressed throughout in terms of ethyl tartrate per 100 grams of solution.

Piperonalsynoxime in Ethyl Tartrate "Twice Distilled."

I. $p = 95·02$. Temperature, 20°. $a = 2·672°$.

T (min.).	$\alpha_D^{20^\circ}$ (100 mm.).	1000 k.
0	+14·11°	—
55	14·012	0·680
185	13·80	0·665
300	13·60	0·706
800	12·955	0·723
1245	12·55	0·704
1505	12·39°	0·685
1705	12·28	0·677
2010	12·125	0·676
2760	11·840	0·686
∞	11·438	—
	Mean	**0·689**

The ethyl tartrate was then redistilled, a first fraction of about one-fifth being rejected, and with the ester thus purified two solutions of the same strength as before were made up and examined polarimetrically with these results :

Piperonalsynoxime in Ethyl Tartrate "Three Times Distilled."

II. $p = 94·97$. Temperature, 20°. $a = 2·946°$.

T (min.).	$\alpha_D^{20^\circ}$ (100 mm.).	1000 k.
0	+14·40°	—
60	14·339	0·346
140	14·257	0·355
250	14·140	0·372
375	13·982	0·382
1140	13·416	0·356
2985	12·546	0·333
4160	12·182	0·332
∞	11·454	—
	Mean	**0·354**

III. $p = 94·95$. Temperature, 20°. $a = 2·948°$.

T (min.).	$\alpha_D^{20^\circ}$ (100 mm.).	1000 k.
0	+14·40°	—
50	14·35	0·352
130	14·266	0·360
430	14·01	0·337
1190	13·396	0·349
1675	13·06	0·362
2600	12·653	0·345
∞	11·452	—
	Mean	**0·351**
	Mean of both series	**0·352**

The mean values of the constant in these two independent experiments differ by less than 1 per cent., which, considering that the total change is something less than 3°, must be regarded as very satisfactory.

It is clear that the third distillation effected a considerable purification, since the value of 1000 k has fallen from 0·689 to 0·352, or almost to one-half. The ethyl tartrate was then redistilled as before and a fourth solution prepared, to which, with the object of hastening the reaction, a drop of alcohol was added. The result was as follows :

Piperonalsynoxime in Ethyl Tartrate "Four Times Distilled."

IV. $p = 94·94$. Temperature, 20°. $a = 2·736°$.

T (min.).	$\alpha_D^{20^\circ}$ (100 mm.).	1000 k.
0	14·18°	—
50	14·16	0·152
105	14·136	0·149
1165	13·744°	0·149
∞	11·444	—
	Mean	**0·150**

The fourth distillation had thus effected a further considerable purification ; the value of *k* was this time rather more than halved, so that the presence of the drop of alcohol can have had very little, if any, accelerating effect. The reaction was so slow that more than three weeks elapsed before the rotation reached a final value. Presumably, continued distillation would reduce the velocity still further, and it would seem that in this procedure we have a test much more delicate than any other for ascertaining the purity of this and probably also other active esters.

These results have two important bearings. They show, firstly, that a set of observations obtained for a certain oxime with one specimen of ethyl tartrate or other ester must only be compared very cautiously with results got by using a different sample of active indicator, and, secondly, that it is not possible to compare with absolute accuracy the velocity of transformation of an inactive substance in one ester, say ethyl tartrate, with its rate of transformation in another ester, say *n*-propyl tartrate, since we have at present no means of deciding when the two esters are of exactly the same degree of purity. This latter consideration applies to our recently published work (*Ber.*, 1907, **40**, 2564), in which we compared the velocity of transformation of anis*syn*aldoxime in several esters. Nevertheless, since the esters used had all been prepared and purified in the same manner, any results obtained by comparison of the data quoted are, doubtless, not far from the truth.

It is clear that a highly purified ester is not very suitable for the study of intramolecular rearrangement by our method, since the experiments take so long to run to completion. We therefore used for the following quantitative experiments with piperonal*syn*oxime, a fresh sample of ethyl tartrate "twice distilled," and, in order to have some standard by means of which our present data may be compared with those given in previous papers, we first determined the velocity of transformation of a specimen of anis*syn*aldoxime twice precipitated as hydrochloride and crystallised, first from methyl alcohol, and then from benzene (m. p. 133°):

Anissynaldoxime in Ethyl Tartrate "Twice [illegible] Distilled."

$p = 95\cdot0$. Temperature, 20°. $a = 3\cdot1$[illegible] ter 68°.

T (min.).	$a_D^{20°}$ (100 mm.).	1000 *k*.	*T* (min.).	$a_D^{20°}$ (100 mm.).	1000 *k*.
0	14·25°	—	375	12·512°	2·10
65	13·816	2·25	450	12·218	2·25
105	13·556	2·30	520	12·182	2·00
185	13·164	2·25	1405	12·264	1·96
245	12·904	2·24	∞	11·062	—
295	12·748	2·15		Mean	[illegible]

The total change of rotation is thus very nearly the same as that ($a = 3·008°$) observed in the experiment with anisaldoxime already described (*Ber.*, 1907, **40**, 2567), but the value of 1000 k (2·17) is greater than that previously found (1·83). This is due to the fact that the ester used in the experiment quoted had been three times distilled, and was therefore somewhat purer than that with which the above data were obtained.

The Influence of Temperature on the Rearrangement of Piperonalsynoxime.

With the above sample of ethyl tartrate (1000 k for anisaldoxime = 2·17), we carried out a number of experiments with piperonal*syn*oxime at different temperatures, commencing at 20° and rising by two degrees each time to 30°, the delicacy of the reaction making it easily possible to proceed by small increments. At each temperature, two solutions of the same concentration (as nearly as possible 5 per cent. of oxime in each case) were examined, the oxime being separately crystallised for each solution and shortly before its preparation, so that the determinations are quite independent.

Temperature, 20°.

I. $p = 94·96$. $a = 2·866°$.

T (min.).	$\alpha_D^{20°}$ (100 mm.).	1000 k.
0	+14·32°	—
40	14·254	0·567
275	13·894	0·586
1130	13·07	0·507
1390	12·892	0·496
1790	12·654	0·486
2605	12·242	0·496
2965	12·116	0·494
4025	11·83	0·501
∞	11·454	—
	Mean	**0·517**

II. $p = 94·95$. $a = 2·866°$.

T (min.).	$\alpha_D^{20°}$ (100 mm.).	1000 k.
0	+14·32°	—
40	14·258	0·542
205	14·004	0·569
310	13·866	0·556
395	13·758	0·552
565	13·558	0·546
1425	12·862	0·499
1740	12·66	0·497
2870	12·184	0·476
3230	12·066	0·478
∞	11·454	—
	Mean	**0·524**

Temperature, 22°.

III. $p = 94·98$. $a = 2·888°$.

T (min.).	$\alpha_D^{22°}$ (100 mm.).	1000 k.
0	+14·44°	—
130	14·232	0·579
175	14·156	0·589
350	13·906	0·584
1185	12·98	0·594
1815	12·566	0·577
2620	12·192	0·579
2725	12·162	0·570
2915	12·10	0·570
3130	12·058	0·556
∞	11·552	—
	Mean	**0·577**

IV. $p = 94·87$. $a = 2·88°$.

T (min.).	$\alpha_D^{22°}$ (100 mm.).	1000 k.
0	+14·44°	—
150	14·204	0·571
255	14·058	0·558
305	13·962	0·596
545	13·66	0·580
1380	12·808	0·606
1455	12·764	0·599
1785	12·562	0·591
2800	12·158	0·561
∞	11·560	—
	Mean	**0·583**

Temperature, 24°.

V. $p = 94 \cdot 925$. $a = 2 \cdot 84°$.

T (min.).	$\alpha_D^{24°}$ (100 mm.).	1000 *k*.
0	+14·53°	—
125	14·254	0·818
230	14·042	0·817
280	13·944	0·825
1295	12·718	0·784
1555	12·566	0·759
1860	12·416	0·733
∞	11·690	—
	Mean	0·789

VI. $p = 94 \cdot 91$. $a = 2 \cdot 84°$.

T (min.).	$\alpha_D^{24°}$ (100 mm.).	1000 *k*.
0	+14·53°	—
115	14·294	0·749
230	14·050	0·806
350	13·828	0·810
535	13·544	0·798
1395	12·670	0·761
1600	12·586	0·768
1675	12·514	0·738
∞	11·690	—
	Mean	0·776

Temperature, 26°.

VII. $p = 94 \cdot 984$. $a = 2 \cdot 798°$.

T (min.).	$\alpha_D^{26°}$ (100 mm.).	1000 *k*.
0	+14·68°	—
70	14·484	1·03
130	14·308	1·09
160	14·224	1·12
287	13·918	1·11
555	13·392	1·11
1355	12·510	1·10
1420	12·440	1·13
∞	11·882	—
	Mean	1·10

VIII. $p = 95 \cdot 01$. $a = 2 \cdot 80°$.

T (min.).	$\alpha_D^{26°}$ (100 mm.).	1000 *k*.
0	+14·68°	—
60	14·490	1·17
170	14·186	1·14
320	13·820	1·14
515	13·428	1·15
1405	12·444	1·14
1520	12·416	1·08
1805	12·272	1·09
∞	11·88	—
	Mean	1·13

Temperature, 28°.

IX. $p = 95 \cdot 01$. $a = 2 \cdot 766°$.

T (min.).	$\alpha_D^{28°}$ (100 mm.).	1000 *k*.
0	+14·78°	—
90	14·43	1·50
146	14·268	1·40
205	14·070	1·44
350	13·702	1·41
510	13·374	1·39
600*	13·210	1·40
800*	12·95	1·35
∞	12·014	—
	Mean	1·41

X. $p = 95 \cdot 02$. $a = 2 \cdot 772°$.

T (min.).	$\alpha_D^{28°}$ (100 mm.).	1000 *k*.
0	+14·78°	—
100	14·374	1·58
140	14·232	1·57
200*	14·080	1·40
380	13·616	1·43
400*	13·590	1·42
500*	13·370	1·45
650	13·100	1·43
∞	12·008	—
	Mean	1·47

Temperature, 30°.

XI. $p = 95 \cdot 01$. $a = 2 \cdot 776°$.

T (min.).	$\alpha_D^{30°}$ (100 mm.).	1000 *k*.
0	+14·90°	—
115	14·304	2·10
200	13·996	1·97
260	13·794	1·95
315	13·648	1·90
380	13·480	1·87
415	13·400	1·87
492	13·240	1·85
∞	12·124	—
	Mean	1·93

XII. $p = 95 \cdot 01$. $a = 2 \cdot 776°$.

T (min.).	$\alpha_D^{30°}$ (100 mm.).	1000 *k*.
0	+14·90°	—
108	14·324	2·15
195	13·988	2·04
290	13·690	1·97
370	13·466	1·94
520	13·158	1·90
600*	13·030	1·86
800*	12·78	1·80
∞	12·124	—
	Mean	1·95

* These values are taken from a curve drawn through the other experimental points.

It will be observed that the two average values of the velocity constant at each temperature agree satisfactorily, the percentage difference between them being respectively 1·3, 0·9, 1·7, 2·9, 3·9, and 1·0. The velocity of the reaction, of course, increases rapidly with rise of temperature, and, as will be seen from the table below, it increases in accordance with the formula suggested by van't Hoff ;

$$a = \frac{T_0 T_1}{T_1 - T_0} \log_e \frac{k_1 T_1}{k_0 T_0},$$

where $a =$ a constant, T_0 and T_1 are absolute temperatures, and k_0 and k_1 the corresponding values of the velocity constant.

Substituting in this equation the values for k_{24} and k_{30}, we find $a = 13620$. Using this value for a, and putting k_{30} for k_1, we obtain for the theoretical value of k at the other temperatures the numbers in the second column below :

Temperature.	1000 k calculated. $a = 13620$. $k_{30} = 1·941$.	1000 k. observed.	Δ.
20°	0·418	0·520	0·102
22	0·574	0·580	0·006
24	(0·782)	(0·782)	—
26	1·063	1·114	0·051
28	1·440	1·440	0·000
30	(1·941)	(1·941)	—

The agreement between the calculated and experimental values is quite satisfactory, except at 20°. That at the lowest temperature the difference is greatest is probably due to the fact that the slight heating which is necessary to dissolve the oxime accelerates the reaction in its initial stage. In the other experiments, the temperature required for bringing about solution is not much higher than that maintained during the reaction, which consequently pursues a normal course.

The above formula has been applied by Ley (*Zeitsch. physikal. Chem.*, 1895, **18**, 387) to the velocity of conversion of acetates of *syn*-oximes into acetates of *anti*-oximes, with somewhat similar results.

Having carried out the above series of experiments, we extended our investigation to some other reactions, for the measurement of the velocity of which our method either might be applied or else is the only one available. The following data relate to a reaction of the latter class.

Velocity of Rearrangement of p-*Iodobenzsyn*aldoxime *in* n-*Propyl Tartrate.*

The oxime melted at 150°, and was not sufficiently soluble in the ester for a 5 per cent. solution to be made up :

$p=97\cdot51$. Temperature, 19·6°. $\alpha=1\cdot507^\circ$.

T (min.).	$\alpha_D^{19\cdot6^\circ}$ (100 mm.).	1000 k.	T (min.).	$\alpha_D^{19\cdot6^\circ}$ (100 mm.).	1000 k.
0	+16·02°	—	2930	+15·05°	0·352
35	16·00	0·368	3180	15·00	0·355
295	15·863	0·374	4050	14·833	0·382
1150	15·513	0·356	4615	14·766	0·386
1450	15·443	0·356	∞	14·513	—
2610	15·13	0·342		Mean	**0·363**

The *n*-propyl tartrate used in this experiment was the same as that in which the transformation of anis*syn*aldoxime and *m*-nitrobenz*syn*-aldoxime had been observed (*Ber.*, 1907, **40**, 2568), so that the constants should be directly comparable. They are:

Substance.	1000 k^{20° in *n*-propyl tartrate.
Anis*syn*aldoxime	1·01
m-Nitrobenz*syn*aldoxime	0·49
p-Iodobenz*syn*aldoxime	0·363

*The Velocity of Transformation of ω-*iso*Nitrotoluene (Phenyl*iso*nitromethane).*

In our first paper, we were able to show that it is possible to follow by our new method the change of the enol-form of formylphenylacetic ester into the more stable aldo-form. Another substance which claims very considerable interest on account of the fact that it exists in two forms which exhibit a somewhat similar relationship is ω-nitrotoluene. The change of ω-*iso*nitrotoluene into ω-nitrotoluene has been followed by Hantzsch and Davidson (*Ber.*, 1896, **29**, 2259) by mixing together solutions of the sodium salt of the former substance and hydrochloric acid, and observing the gradual diminution in conductivity of the solution; also by following a slow change in the apparent molecular weight as determined by the cryoscopic method in benzene (*loc. cit.*, 2264), and, further, by the application of the ferric chloride reaction. By none of these methods, however, has an attempt been made to obtain a value for the velocity constant. This seemed therefore an interesting case to which to apply our method. We prepared some ω-*iso*nitrotoluene from benzyl iodide and freshly-precipitated silver nitrite according to Hollemann (*Rec. trav. chim.*, 1894, **13**, 403) and Hantzsch (*Ber.*, 1896, **29**, 699, 2251). Only a small yield (0·5 gram, m. p. 75°) was obtained, a considerable quantity of substance having been lost in purification.

A solution containing about 10 per cent. of ω-*iso*nitrotoluene (6 grams in all) was made up with some of the same *n*-propyl tartrate as used in the previous experiment, and this was examined in a 50 mm. tube in the polarimeter. The result was as follows:

$p = 90\cdot19$. Temperature, 19·5°. $a = 0\cdot907°$.

T (min.).	$a_D^{19\cdot5°}$ (50 mm.).	1000 k.
0	+7·82°	—
50	7·70	2·83
155	7·513	2·66
375	7·290	2·34
490	7·173	2·55
1340	6·913	—
∞	6·913	—
	Mean	2·59

The total difference of rotation (0·907°, using only a 50 mm. tube) thus induced by the change from one form of the inactive substance to the other is very considerable, although not so great as with the oximes. The reaction is apparently unimolecular, and the value of the constant is satisfactory. The velocity of transformation is more than twice as great as that of anis*syn*aldoxime in the same active ester.

The Isomerism of Ammonium Thiocyanate and Thiocarbamide.

We have also examined some other isomeric substances of a more easily accessible type. For the purpose, we used an aqueous solution of ethyl tartrate of concentration $p = 50$. It had $a_D^{20\cdot2}$ (100 mm.) +9·73°.

A solution of 1 gram of thiocarbamide and 10 grams of this solution had a_D^{19} (100 mm.) +10·006°. The thiocarbamide therefore raises the rotation of the solution slightly.

An exactly similar solution of ammonium thiocyanate had $a_D^{19\cdot2}$ (100 mm.) +5·26°.

The effect of isomerism in these compounds is thus very striking indeed. The rotation of the former solution is practically double that of the latter, and this alteration is really enormous considering that it is brought about by difference in constitution of less than 10 per cent. of inactive substance.

The rotation of neither solution altered on standing, but on heating obvious decomposition ensued.

These experiments indicate a simple means of following the conversion of ammonium thiocyanate into thiocarbamide, but, since the course of that reaction has already been carefully examined (Waddell, *J. Physical Chem.*, 1898, **2**, 523; Reynolds and Werner, Trans, 1903, **83**, 1), it did not seem necessary to do more than satisfy ourselves as to the possibility of applying our method.

Small quantities (about 2 grams) of ammonium thiocyanate and thiocarbamide were heated in sealed test-tubes for some two and a-half hours to about 170° in a Lothar Meyer air-bath. A solution of each substance was then made up by dissolving 1 gram in 10 grams of the aqueous ethyl tartrate solution:

		Rotation before heating.
After heating, the thiocyanate gave a solution of $\alpha_D^{19\cdot4}$ (100 mm.)	$+6\cdot576°$	$+5\cdot26°$
,, ,, thiocarbamide ,, ,, $\alpha_D^{19\cdot9}$,,	$7\cdot192°$	$10\cdot006°$

The thiocarbamide was thus being transformed more rapidly than the thiocyanate. The rotations were approaching a common value, but equilibrium had not yet been reached.

A second experiment was carried out, the substances being kept fused for about twelve hours at 160—170°, and then dissolved as before in the ethyl tartrate solution. The rotations then were

Thiocyanate solution, $\alpha_D^{20\cdot1}$ (100 mm.) 7·212°.
Thiocarbamide solution, $\alpha_D^{19\cdot8}$ (100 mm.) 7·112°.

Equilibrium had thus practically been attained,* and calculating the proportion of thiocyanate converted into thiocarbamide on the assumption that change of rotation is directly proportional to quantity of substance transformed, which may not be quite correct, the above experiment gives a formation from ammonium thiocyanate of 40 per cent. of thiocarbamide. Considering the rough character of the experiment, no special precautions whatever having been taken, it is not surprising that the result is not in close accord with Reynolds' accurate value of 24·76 per cent.

The Isomerism of Ammonium Cyanate and Carbamide.

We next tried similar experiments with ammonium cyanate and carbamide. A solution of ammonium cyanate was prepared by mixing concentrated solutions of potassium cyanate and ammonium sulphate. The precipitated potassium sulphate was filtered off, and the cyanate solution mixed with ethyl tartrate. Unfortunately, this precipitated more potassium sulphate, and the solution had to be further diluted. The concentration of the solution used was, as regards ethyl tartrate, $p=25$, and as regards ammonium cyanate, approximately $p=4\cdot5$. This mixture was then examined in the polarimeter at 20°, and yielded the following data:

---

* According to Reynolds and Werner (*loc. cit.*, p. 4) equilibrium is attained in a much shorter time, about 45 minutes at 170°.

Transformation of Ammonium Cyanate into Carbamide.

T (min.).	$a_D^{20°}$ (200 mm.).	T (min.).	$a_D^{20°}$ (200 mm.).
0	+10·56°	1680	+13·12°
35	10·62	1900	13·27
55	10·67	2780	13·83
210	10·85	4570	14·40
505	11·45	∞	14·55

The rotation of the solution thus increases slowly and to a considerable extent. The numbers do not give a constant when calculated by the formula for reactions of the first order, which is in accordance with the known course of the reaction (Walker, with Hambly, Kay, and Wood, Trans., 1895, **67**, 746; 1897, **71**, 489; 1898, **73**, 21). Our data are insufficient to allow of the application of the formula for reactions of the second order, but the experiment recorded is quite sufficient to show that our method would have been valuable in this case also had the transformation not already been thoroughly investigated by other means.

That the reverse change of carbamide into ammonium cyanate can also be followed in the polarimeter is shown by the following experiment. An aqueous solution was made up of $p = 41·8$, relative to ethyl tartrate, and $p = 11·1$, relative to carbamide. It gave the following result at 26°:

T (min.).	$a_D^{26°}$ (200 mm.).
15	+20·044°
70	19·988
260	19·814

The rotation thus diminishes with lapse of time, but the diminution is slight.

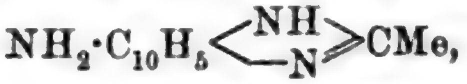
The experiments recorded here show that the solvent influence of two isomeric substances on the rotation of ethyl tartrate may differ very considerably, and that on this fact may be based a method for determining constitution or for measuring the velocity of intramolecular reactions in inactive compounds. We are continuing our investigation of the subject in various directions.

THE UNIVERSITY,
GLASGOW.

CIV.—*Contributions to the Chemistry of the Amidines. Part II. Anilinobenzoxazole and the Supposed Anilodihydrobenzoxazole.*

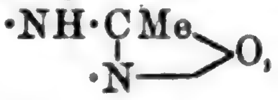
By GEORGE YOUNG and ALBERT ERNEST DUNSTAN.

As the existence of isomerides differing from each other in the position of a hydrogen atom, which in other similar compounds is found to be so mobile that only one of the two, or only a mixture of the two, possible substances can be obtained, is of the utmost importance for the theory of the phenomena commonly grouped together under the name of tautomerism, it is desirable that doubtful cases of such isomerism should be carefully re-investigated. In a previous paper, in conjunction with W. H. Oates (Trans., 1901, **79**, 660), one of us drew attention to two such doubtful cases in the amidine group, and expressed the opinion that further evidence was necessary before the constitution of the substances concerned could be considered as established. The re-investigation of these substances, then undertaken, has been unavoidably delayed, but in the meantime the doubt expressed as to the isomerism of the aminomethyl-α-naphthiminazole has been justified by O. Fischer, who recently brought forward evidence (*J. pr. Chem.*, 1907, [ii], **75**, 88) showing that, whilst Markfeldt's compound (*Ber.*, 1898, **31**, 1174) has the structure



$$NH_2\cdot C_{10}H_5{<}\begin{matrix}NH\\N\end{matrix}{>}CMe,$$

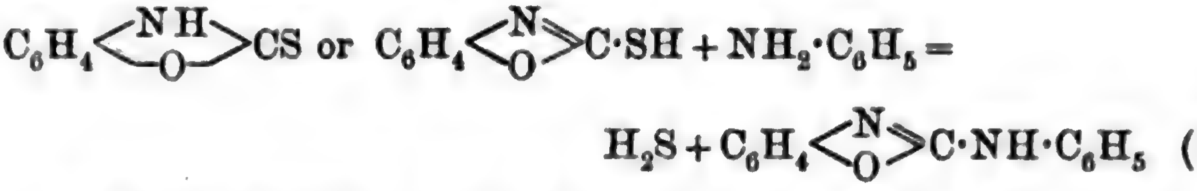
the supposed isomeride (Meldola and Eynon, Trans., 1900, **77**, 1159) is probably an oxygenated compound containing the grouping



$$\begin{matrix}\cdot NH\cdot CMe\\ \cdot N\end{matrix}{>}O,$$

instead of the amidine grouping $\begin{matrix}\cdot NH\\ \cdot N\end{matrix}{>}CMe$, the oxygen atom having been mistaken for a molecule of water of crystallisation. In this paper, we deal now with the other case to which attention was drawn.

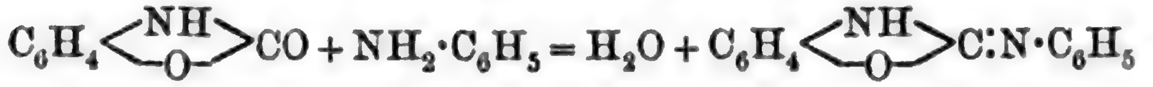
Kalckhoff, on heating 1-mercaptobenzoxazole with aniline at the boiling point of the latter, obtained a product, melting at 173°, which he considered to be 1-anilinobenzoxazole (*Ber.*, 1883, **16**, 1825), formed according to the scheme:



$$C_6H_4{<}\begin{matrix}NH\\O\end{matrix}{>}CS \text{ or } C_6H_4{<}\begin{matrix}N\\O\end{matrix}{>}C\cdot SH + NH_2\cdot C_6H_5 =$$
$$H_2S + C_6H_4{<}\begin{matrix}N\\O\end{matrix}{>}C\cdot NH\cdot C_6H_5 \quad (I).$$

The same substance was also obtained by heating 2-hydroxyphenylthiocarbamide with aniline, and by heating 2-hydroxy-*s*-diphenylthiocarbamide alone or with mercuric oxide.

Some years later, Chelmicki heated 1-keto-1 : 2-dihydrobenzoxazole with aniline in a sealed tube at 200—210°, and obtained a small amount of white, brittle needles, which melted and decomposed at about 230° (*J. pr. Chem.*, 1890, [ii], **42**, 440). Chelmicki ascribed to his product the constitution of 1-anilo-1 : 2-dihydrobenzoxazole, and considered it to be formed according to the scheme:

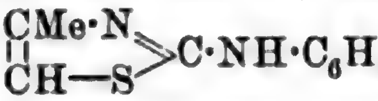
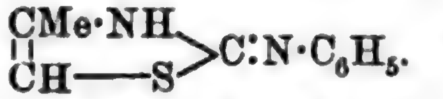


$$C_6H_4{<}\genfrac{}{}{0pt}{}{NH}{O}{>}CO + NH_2\cdot C_6H_5 = H_2O + C_6H_4{<}\genfrac{}{}{0pt}{}{NH}{O}{>}C{:}N\cdot C_6H_5 \quad \text{(II).}$$

Kalckhoff's and Chelmicki's substances appear therefore as a pair of isomeric amidines differing in the position of an *N*-hydrogen atom, since they contain the groups:

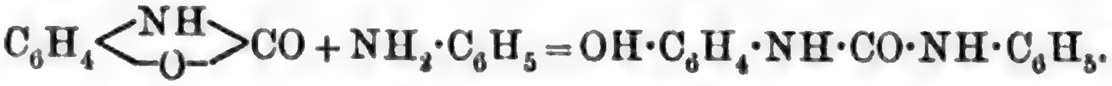
$$\cdot N{:}C\cdot NH\cdot C_6H_5 \text{ and } \cdot NH\cdot C{:}N\cdot C_6H_5$$

respectively. This seemed an extremely doubtful case of such isomerism; both substances were prepared at high temperatures, and purified by treatment with hot, dilute hydrochloric acid to remove unchanged aniline and thereafter by recrystallisation from hot alcohol, processes well calculated to effect isomerisation of one or other of the two forms if the *N*-hydrogen atom is capable of intramolecular wandering. On the other hand, the tautomerism of the amidines is not yet settled beyond question, and it is still possible that two such isomerides may be both stable. The results described in this paper show that the particular case under discussion is not one of isomerism.

We can confirm in all respects the statements of Kalckhoff as to the nature of the product obtained on heating 1-mercaptobenzoxazole with aniline. It has feeble basic properties, and on analysis gives figures agreeing with those required by a substance of the formula $C_{13}H_{10}ON_2$. We have prepared from it an acetyl derivative which on hydrolysis is converted again into the anilino-compound, or, depending on the conditions, gives aniline and 1-keto-1 : 2-dihydrobenzoxazole. These properties of the substance and the methods employed for its preparation do not suffice to distinguish between a compound having the formula (I), as given by Kalckhoff, and one of the formula (II), ascribed by Chelmicki to his product. It was shown by one of us, in conjunction with S. I. Crookes (Trans., 1906, **89**, 59), that 2-anilinomethylthiazole has the constitution  $\begin{array}{l}CMe\cdot N\\ \|\\ CH-S\end{array}{>}C\cdot NH\cdot C_6H_5$, and not the isomeric form  $\begin{array}{l}CMe\cdot NH\\ \|\\ CH\text{——}S\end{array}{>}C{:}N\cdot C_6H_5$. The analogy of this substance to anilinobenzoxazole makes it probable that the latter has the corresponding constitution containing the grouping $\begin{matrix}\cdot C\cdot N \\ \| \\ \cdot C\cdot O\end{matrix}\!>\!C\cdot NHPh$, and we therefore incline to Kalckhoff's formula for his product.

Whilst we confirm the results of Kalckhoff, our study of the interaction of aniline and 1-keto-1 : 2-dihydrobenzoxazole has led to a conclusion entirely different from that put forward by Chelmicki. We found that, as stated by that author, the substances interact at 200—210°, forming a product which, after removal of unchanged aniline, crystallises from alcohol in needles, melting at about 230°. The figures obtained on analysis, however, did not agree with those required by a substance of the formula $C_{13}H_{10}ON_2$ ($C = 74{\cdot}2$; $H = 4{\cdot}8$; $N = 13{\cdot}3$ per cent.), but approximated closely to those required by the formula $C_{13}H_{12}ON_2$ ($C = 73{\cdot}6$; $H = 5{\cdot}7$; $N = 13{\cdot}2$ per cent.). It is evident that a nitrogen estimation (the only analysis quoted by Chelmicki) could not distinguish between these two formulæ, but that a carbon-hydrogen estimation should be decisive.

The formula $C_{13}H_{12}ON_2$ is that of *s*-diphenylcarbamide. This might be formed by the interaction of aniline and 1-keto-1 : 2-dihydrobenzoxazole in two ways, the first stage of the two reactions being the same:

I. 

$$C_6H_4\begin{matrix}\diagup NH \diagdown \\ \diagdown\; O \;\diagup\end{matrix}CO + NH_2{\cdot}C_6H_5 = OH{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_6H_5.$$

IIa. $$2\,OH{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}NHPh = OH{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}OH + C_6H_5{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_6H_5.$$

IIb. $$OH{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}OH + NH_2{\cdot}C_6H_5 = OH{\cdot}C_6H_4{\cdot}NH_2 + C_6H_5{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_6H_5.$$

The suspicion that in these equations lay the explanation of Chelmicki's reaction was confirmed, as a mixture of the product, m. p. 230°, with an equal amount of pure *s*-diphenylcarbamide, m. p. 236°, melted at about 234—235°. Moreover, we found later that repeated recrystallisation of the product from alcohol gradually removes a small amount of a reddish-white impurity, the melting point of the substance rising slowly to 235—236°. It is evident then that Chelmicki's supposed 1-anilo-1 : 2-dihydrobenzoxazole was nothing more or less than *s*-diphenylcarbamide, containing probably traces of some decomposition product of *s*-dihydroxydiphenylcarbamide formed according to scheme II*a*, and hence this case of the supposed isolation of isomeric amidines differing in the position of the *N*-hydrogen atom must be deleted from the record as founded on a misconception as to the nature of one of the so-called isomerides.

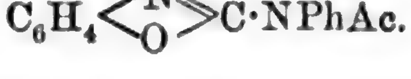
If Chelmicki's product was *s*-diphenylcarbamide, it is difficult to understand his statement that on hydrolysis with concentrated hydrochloric acid it yields *o*-aminophenol. It might be urged that the original product of the reaction is in reality anilodihydrobenzoxazole, and that during our process of purification this underwent a change consisting in the first place of hydrolysis to *o*-hydroxy-*s*-diphenylcarbamide, $OH\cdot C_6H_4\cdot NH\cdot CO\cdot NH\cdot C_6H_5$, and in the second of the reaction II*a*. But it seems scarcely probable that the five-atom ring of anilodihydrobenzoxazole would undergo resolution much, if any, more readily than the condensation ring of Kalckhoff's anilinobenzoxazole, and this remains unchanged when the substance is boiled with aqueous or absolute alcohol or with dilute or concentrated hydrochloric acid. Moreover, the purification which takes place with so much difficulty by Chelmicki's method is readily effected by washing the product with benzene.

We have obtained also *s*-di-*p*-tolylcarbamide by heating 1-keto-1 : 2-dihydrobenzoxazole with *p*-toluidine.

On treating his product with calcium hypochlorite in acetic acid solution, Chelmicki obtained a chlorinated substance, melting at 276°, to which he ascribed the formula $C_{13}H_8ON_2Cl_2$. No details are given of how this reaction was carried out, and we have been unable to obtain a product having the melting point quoted by Chelmicki, but we have found that, under varying conditions, the reaction leads to the formation of mixtures of monochloro-, dichloro-, and trichloro-*s*-diphenylcarbamide. Of these, we have isolated only the trichloro-derivative, which melts at 262°. For purposes of comparison we have compared di-*p*-chloro-*s*-diphenylcarbamide by heating *p*-chlorophenylcarbamide with *p*-chloroaniline, and have found it to melt at 289°. As di-*p*-chloro-*s*-diphenylcarbamide forms the trichloro-*s*-diphenylcarbamide, m. p. 262°, when treated with calcium hypochlorite in acetic acid solution, the latter is probably the 2 : 4 : 4′-trichloro-compound. Chelmicki's chlorinated product was probably a mixture of the dichloro-*s*-diphenylcarbamide with smaller amounts of the other chloro-derivatives.

EXPERIMENTAL.

1-*Acetylanilinobenzoxazole*,



$$C_6H_4{<}\overset{N}{\underset{O}{}}{>}C\cdot NPhAc.$$

This substance was prepared by boiling 1-anilinobenzoxazole, m. p. 173°, with acetic anhydride in a reflux apparatus. It crystallises from a mixture of benzene and light petroleum in sheaves of white needles, which melt at 91° :

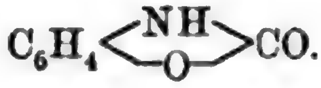
0·1986 gave 0·5188 CO_2 and 0·9894 H_2O. C = 71·2 ; H = 5·00.

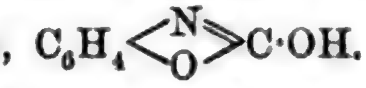
$C_{15}H_{12}O_2N_2$ requires C = 71·4 ; H = 4·76 per cent.

A mixture of this acetyl derivative with the acetyl derivative of 1-keto-1 : 2-dihydrobenzoxazole, which melts at 95° (Bender, *Ber.*, 1886, **19**, 2269), melted at about 70°.

When boiled with dilute hydrochloric acid, 1-acetylanilinobenzoxazole is hydrolysed, forming 1-anilinobenzoxazole, but if heated with concentrated hydrochloric acid and evaporated to dryness on the water-bath it yields aniline and 1-keto-1 : 2-dihydrobenzoxazole, melting at 138—139°. The identity of the anilinobenzoxazole and of the ketodihydrobenzoxazole with specimens of these substances prepared by the synthetical reactions was established by the method of mixed melting points; the aniline was recognised by the bleaching-powder test.

1-*Keto*-1 : 2-*dihydrobenzoxazole*, $C_6H_4<\substack{NH\\O}>CO$.



Sandmeyer, who prepared this substance by fusing *o*-aminophenol with carbamide, found it to melt at 137—138° (*Ber.*, 1886, **19**, 2656), whilst somewhat later (*J. pr. Chem.*, 1890, [ii], **41**, 387), Leuckart recorded the melting point as 141—142°. Seidel (*J. pr. Chem.*, 1890, [ii], **42**, 445) observed that the substance separates from water in glistening crystals, which on exposure to air become dull, changing into small needles, and considered that this behaviour pointed to the transient existence of a mobile, lactim form,  $C_6H_4<\substack{N\\O}>C\cdot OH$. We have found, however, that this change in the appearance of the crystals is merely the accompaniment of a loss of water of crystallisation. We prepared the substance by Sandmeyer's method, and, after repeated recrystallisation of the product from boiling water in presence of animal charcoal, and finally from very dilute hydrochloric acid, obtained it in glistening, white, flat needles or plates. These melt at 97—98°, and when more highly heated rapidly lose a molecule of water, the substance solidifying and again melting at about 137°. The crystals lose the water of crystallisation also when dried over sulphuric acid in a vacuum, or more slowly and less completely when exposed to air:

0·2654, dried at 100—105°, lost 0·0332. $H_2O = 12·5$.
0·2116, dried over sulphuric acid, lost 0·0244. $H_2O = 11·5$.
$C_7H_5O_2N,H_2O$ requires $H_2O = 11·8$ per cent.

The high value for the water of crystallisation as determined at 100—105° resulted probably from loss of substance by volatilisation, as anhydrous ketodihydrobenzoxazole on prolonged heating at about 120° sublimed in delicate, white needles, in which form it is obtained also on recrystallisation from dry benzene. The anhydrous substance melts at 137—138°. It does not show any tendency to absorb water on exposure to moist air, but on recrystallisation from dilute hydrochloric acid yields the hydrated crystals, melting at 97—98°:

0·2410 gave 21·0 c.c. nitrogen at 14° and 766 mm. N = 10·5.

$C_7H_5O_2N$ requires N = 10·4 per cent.

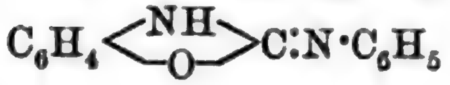
Anhydrous ketodihydrobenzoxazole remains unchanged when heated in boiling nitrobenzene.

Action of Aniline on 1-*Keto*-1 : 2-*dihydrobenzoxazole.*

The product of the action of aniline on 1-keto-1 : 2-dihydrobenzoxazole at 200—210° in a sealed tube was obtained by Chelmicki in only very small yields. We have found that it can be isolated in a 10 per cent. yield, calculated for the formation of *s*-diphenylcarbamide according to equations I and II*a* as given in the introduction, if the anhydrous oxy-compound is introduced into a dry tube, an excess of aniline distilled directly into the tube, and precautions taken against the entrance of moisture during the process of sealing. The product, after being treated repeatedly with hot dilute hydrochloric acid, as directed by Chelmicki, and crystallised once from alcohol, formed small, slightly dark needles, which melted at about 230°, and gave the following figures on analysis :

0·0799 gave 0·2152 CO_2 and 0·0425 H_2O. C = 73·5 ; H = 5·91.

$CO(NH\cdot C_6H_5)_2$ requires C = 73·6 ; H = 5·66 per cent.



$C_6H_4<\!\overset{NH}{\underset{O}{}}\!>C{:}N\cdot C_6H_5$ requires C = 74·2 ; H = 4·76 per cent.

After repeated recrystallisation from hot alcohol, as also after treatment of the crude substance with benzene, followed by recrystallisation from alcohol, the product crystallised in small, white, brittle needles, or from hot glacial acetic acid in long needles, melting at 235—236°. The melting point was not altered by admixture of *s*-diphenylcarbamide prepared from phenylcarbamide and aniline.

Action of Bleaching Powder on s-Diphenylcarbamide.

Trichloro-s-diphenylcarbamide, $C_6H_3Cl_2\cdot NH\cdot CO\cdot NH\cdot C_6H_4Cl$.

This substance is obtained when *s*-diphenylcarbamide is dissolved in hot glacial acetic acid, and the solution poured into a solution of calcium hypochlorite in dilute acetic acid. The product separates as a voluminous, flocculent precipitate, which, on crystallisation from ethyl acetate, forms tufts of small, white needles, melting when heated in a sealed capillary tube at 262°. If rapidly heated in an open capillary tube, the substance volatilises without melting :

0·0708 gave 0·0961 AgCl. Cl = 33·6.

$C_{13}H_9ON_2Cl_3$ requires Cl = 33·7 per cent.

p-*Chlorophenylcarbamide*, $C_6H_4Cl\cdot NH\cdot CO\cdot NH_2$.

p-Chlorophenylcarbamide was prepared by adding a solution of potassium cyanate to *p*-chloroaniline dissolved in dilute acetic acid. It crystallises from water in clusters of white needles, which melt at 212°, decomposing with formation of the *s*-disubstituted carbamide. The melting point varies to some extent with the rate of heating (compare Young and Clark, Trans., 1897, **71**, 1200):

0·1956 gave 0·1624 AgCl. Cl = 20·5.
C_7H_7ONCl requires Cl = 20·8 per cent.

p-Chlorophenylcarbamide is soluble in ether and in concentrated acids, from which it is reprecipitated on dilution with water. When heated alone above its melting point, or when boiled with *p*-chloroaniline, it forms di-*p*-chloro-*s*-diphenylcarbamide,

$$C_6H_4Cl\cdot NH\cdot CO\cdot NH\cdot C_6H_4Cl.$$

This crystallises from ethyl acetate in small, white needles, which melt at 289° when heated in a sealed capillary tube. Beilstein and Kurbatoff, who prepared di-*p*-chloro-*s*-diphenylcarbamide by the action of iodine on di-*p*-chloro-*s*-diphenylthiocarbamide (*Annalen*, 1875, **176**, 51), stated that their preparation partly decomposed and volatilised at 270°. We have observed that, if heated in an open capillary tube, the dichloro-derivative commences to volatilise, and then partly melts at temperatures between 270° and 285°, depending on the rate of heating:

0·1538 gave 0·1535 AgCl. Cl = 24·7.
$C_{13}H_{10}ON_2Cl_2$ requires Cl = 25·2 per cent.

s-*Di*-p-*tolylcarbamide*, $C_7H_7\cdot NH\cdot CO\cdot NH\cdot C_7H_7$.

This substance was prepared by boiling *p*-tolylcarbamide with *p*-toluidine, and also by heating 1-keto-1 : 2-dihydrobenzoxazole with *p*-toluidine in a sealed tube at 250°. After being washed with dilute hydrochloric acid, the products were crystallised from hot alcohol. Both specimens formed white crystals, which melted separately or when mixed together at 265°. The melting point of *s*-di-*p*-tolylcarbamide has been given by Maly as 263° (*Jahresber.*, 1869, 638), and by Michler (*Ber.*, 1876, **9**, 710) and by Weith (*ibid.*, 821) as 256°.

The following figures were obtained on analysis of a specimen of *s*-di-*p*-tolylcarbamide prepared from ketodihydrobenzoxazole:

0·1536 gave 15·1 c.c. of nitrogen at 17° and 761 mm. N = 11·6.
$C_{15}H_{16}ON_2$ requires N = 11·7 per cent.

One of us (G. Y.) takes this opportunity to thank the Research Fund Committee for a grant from which part of the expense of this work has been defrayed, and the Managers of the Royal Institution for permitting him to work in the Davy-Faraday Research Laboratory.

Davy-Faraday Laboratory,
Royal Institution.

Technical College,
East Ham.

CV.—*The Relation between Dielectric Constant and Chemical Constitution. Part I. Stereoisomeric Compounds.*

By Alfred Walter Stewart (Carnegie Research Fellow).

The many interesting results obtained from the study of the refractive indices of organic compounds have led several investigators to hope that an examination of the dielectric constants would prove even more valuable, and the number of workers in this field has been considerable. A fairly complete bibliography of the subject has been compiled by Mathews (*J. Physical Chem.*, 1905, 9, 667).

When the actual experimental data at our disposal are examined, however, the comparable results are not really so numerous as they appear at first sight to be. In the first place, various workers on the physical side have utilised impure materials, such as sealing wax, bone-oil, and oil of turpentine; and even when pure materials were employed many of the results are useless for comparison purposes. For example, since the presence of absorption bands in the electric spectrum of a compound causes anomalies in the value of the dielectric constant of the substance for certain wave-lengths, it follows that all strongly absorbent substances are of little value from the point of view of the relation between dielectric constant and chemical constitution. This at once excludes all the hydroxylic compounds, for, as Drude has shown, they possess a strong absorptive power.

For the purpose of comparison, therefore, we are restricted to non-hydroxylic and other non-absorbent compounds, and of such substances not very many complete homologous series have been investigated. In the present series of papers, it is proposed to examine the dielectric constants of homologous series of aliphatic esters, acid anhydrides, acid chlorides and bromides, esters of chloro- and bromo-acids, and some halogen derivatives, and from this material to endeavour to discover some relation between the constitution of a compound and its electric refractive index.

Before entering on the examination of these compounds, however, it seemed advisable to find how far the dielectric constants of substances could be influenced by a change in configuration, as, if this exercised any influence, its effect might have to be taken into account in some of the later papers. With this object in view, various active and racemic bodies were examined, but, as far as can be seen, no marked difference in dielectric constant could be found.

The apparatus used was that described by Drude (*Zeitsch. physikal. Chem.*, 1897, **23**, 282; 1902, **40**, 635), and was made by W. Schmidt, of Giessen. The only modification introduced was that, instead of soldering the copper wires into the brass tubes as described by Drude, they were held in place by two binding screws. This modification is useful, as it enables the zero of the apparatus to be set at any point on the scale. The exciter when in the paraffin bath yields waves of sixty-three centimetres length. The vacuum tube used was one containing a mixture of neon and mercury vapour, which was kindly lent to me by Professor Collie. I had previously used a carbon dioxide tube furnished by the Marconi Company, but the results obtained with it were, of course, in no way comparable to those given by the neon. The coil employed was an Apps-Newton commercial one, giving a four-inch spark. It was usually run with a six-volt current. The condenser was one of the plate form described by Drude.

All substances were carefully purified before being examined. The condenser was in each case filled to the mark with a substance, and allowed to stand until it had reached the temperature of the room. In all cases given in the present paper, this temperature was 20°. At least ten readings were taken, and when these differed by more than half a millimetre, ten more observations were made. In cases of doubt, the condenser was refilled several times and the observations compared. The zero was taken by filling the condenser itself with mercury, not by putting in a copper wire instead of the condenser.

The following are the results obtained:

	ϵ.
Ethyl tartrate *	4·50
Ethyl racemate *	4·50

The active form showed a much stronger absorption than the racemic isomeride. This seems to point to the hydroxyl groups being in some way involved in the formation of the racemic compound:

	ϵ.
d-Limonene	2·36
Dipentene	2·30

---

* For these substances, I am indebted to Miss E. C. Payne and Mr. W. R. G. Bye, who kindly prepared very pure specimens for me.

There is a slight difference between these two substances, but it is hardly sufficient to prove much. Taken in conjunction with the other results, it does not suffice to establish a difference between the active and racemic forms:

	ϵ.
d-Pinene	2·60 ?
l-Pinene	2·70
i-Pinene	2·75

The readings obtained for *d*-pinene were not very sharp; *l*-pinene and *i*-pinene have practically the same value. The inactive substance was prepared by mixing equal quantities of the active isomerides:

	ϵ.
d-Camphene	2·75
l-Camphene	2·75
i-Camphene	2·75

All three forms were examined in the solid state. To ensure accuracy, each was melted and allowed to solidify again in an interval between two sets of readings.

With these results should be compared those of Drude (*Zeitsch. physikal. Chem.*, 1897, **23**, 310) and Walden (*ibid.*, 1903, **46**, 176) in the cases of *i*- and *l*-malic esters:

	ϵ.	
l-Malic ester	9·3	(Walden, 20°)
i-Malic ester	10·0	(Drude, 18°)

The difference between these results might quite well be due to the difference between the temperatures at which the observations were made.

Finally, the *d*- and *l*-forms of cocaine were examined. These, of course, are not optical antipodes:

	ϵ.
d-Cocaine	3·05
l-Cocaine	3·10

Both substances were examined in the solid state with the same precautions as in the case of the camphenes.

From these results, it follows that the spacial arrangement of atoms has no marked influence on the dielectric constant of substances. Any difference between the isomeric forms is to be found in a comparison of their absorption powers, but even this was noticed only in the case of the tartrates.

In conclusion, the author wishes to express his thanks to Professor Collie, Professor Inglis, and Assistant-Professor Smiles for the interest they have taken in the work, and to the Chemical Society for a grant towards the cost of this series of researches.

THE ORGANIC CHEMISTRY LABORATORY,
UNIVERSITY COLLEGE,
LONDON.

CVI.—*An Apparatus for Determining the Specific Inductive Capacity of Organic Liquids.*

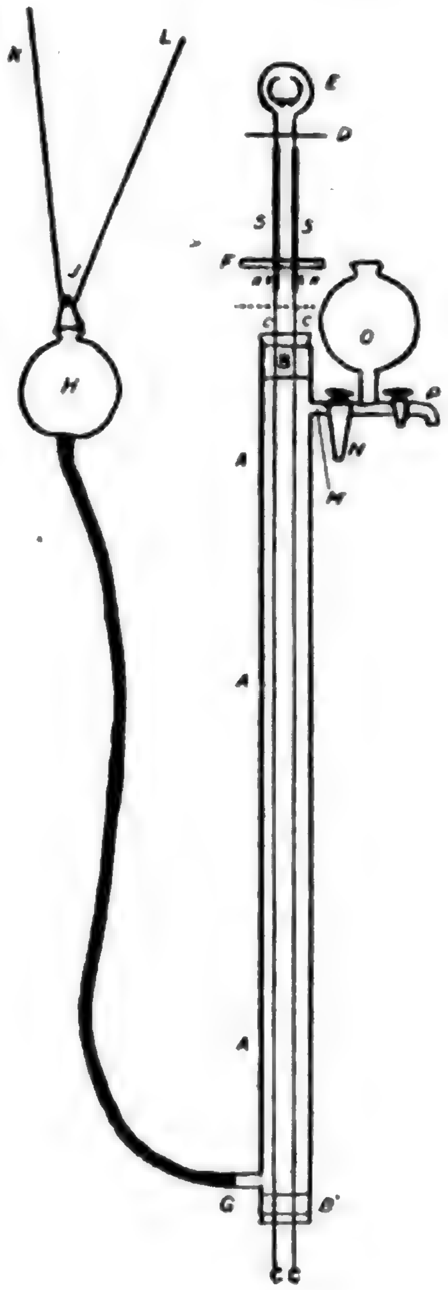
By ALFRED WALTER STEWART (Carnegie Research Fellow).

ABOUT ten years ago, Drude (*Zeitsch. physikal. Chem.*, 1897, **23**, 267) described a method for measuring the specific inductive capacities of organic substances and of solutions by means of Hertzian waves. In one form, his apparatus consisted of an exciter (producing the electric vibrations by means of a spark-gap under petroleum), a secondary wire circuit, with one fixed bridge near the exciter, and a movable one further off, a high vacuum tube to indicate nodes or loops in the vibrations, and a trough containing the liquid the dielectric constant of which it was desired to obtain. Behind the fixed bridge, the wire circuit passed through the trough, and the wave-lengths of the Hertzian waves were measured in air and in the liquid simply by moving the bridge up and down in the trough (thus lengthening or shortening the circuit) and noting the effect on the vacuum tube which is laid across the wires of the secondary circuit outside the trough.

The three chief defects of this method are: (1) the large quantity of liquid which it requires, namely, 250—750 c.c.; (2) the impossibility of keeping the apparatus at a given temperature without introducing an element of clumsiness into it; and (3) the imperfect contact between the movable bridge and the wires of the secondary circuit, which leads to slight sparking and hence to uneven lighting of the vacuum tube. With a view to eliminating these defects, the following apparatus was devised.

The trough of the Drude apparatus is replaced by a jacketed tube, *AAA* (jacket omitted in figure for sake of clearness), graduated in millimetres. This is placed vertically, and closed at both ends by rubber corks, BB^1, through which pass thin wires of iron or nickel, *CC*, kept taut and placed parallel to each other about 1 cm. apart. Just above the cork, at the dotted line in the figure, these wires are bent at right angles and inserted into two 20 cm. tubes of nickel or German silver, *SS*, in which they are retained by the binding-screws, *RR*. The other ends of the tubes *SS* are attached to the circular part of the secondary circuit which surrounds the exciter, *E*, as shown in the figure. The bridge, *D*, and the vacuum tube, *F*, are placed across the circuit as shown in the figure.

At the bottom of the graduated tube, *AAA*, a side tube, *G*, leads to the mercury reservoir, *H*. This tube should be as wide as possible in order to avoid lag in the mercury levelling. The mercury reservoir is furnished with a coarse and a fine adjustment for levelling it. *J* is a pulley through which a cord passes. At *K* this cord is attached to a fine rack and pinion adjustment, whilst the end, *L*, lies in a clamp. To adjust the mercury level, the end *L* is unclamped, and the mercury reservoir moved up and down until the approximate level is reached; *L* is then clamped, and the fine adjustment made from *K*. By this means, maxima or minima in the glow of the vacuum tube can be sharply and easily read off.



The introduction of the liquid to be measured is provided for in the upper part of the apparatus. *M* is a side tube connecting the graduated tube with the bulb, *O*. *N* is a two-way tap, and *P* an ordinary tap. The mercury is run up into the neck of the bulb, *O*, into which the liquid is then poured; and by sinking the mercury level, the liquid can be carried down into the graduated tube. The two-way tap, *N*, may serve to introduce gases as well as liquids into the apparatus.

Before use, the apparatus must be calibrated by the aid of the mixtures of known specific inductive capacity given by Drude (*Zeitsch. physikal. Chem.*, 1897, **23**, 288), and a curve must be drawn showing the relation between scale reading and dielectric constant. In practice, it is well to bring the zero of the apparatus always to the same point; or, in other words, to run the mercury up to the cork, *B*, and then so adjust *CC* by means of the binding-screws, *RR*, that the tube, *F*, is glowing most brightly. This indicates that the first node of the Hertzian waves is just inside the cork, *B*, where the graduation of the tube begins.

With regard to the size of the graduated tube, in the author's experimental apparatus this was made 3 cm. in diameter and 50 cm. long, but this is much larger than is actually necessary.

The length of the tube need not be greater than half the wavelength in air of the vibrations employed; in most cases a length of 30 cm. should suffice. Where compactness is no object, however, longer tubes may be employed, as then two sets of readings can be taken in the same tube. Even with a 30 cm. tube, this is possible if the liquid which is being measured has a high specific inductive capacity. The diameter of the tube also may be reduced if necessary, so that it would be possible to reduce the amount of liquid required for a measurement to 70 or 80 c.c., in the case of a low dielectric constant, or even less in the case of a high one. The bulbs, *H* and *O*, of course, must be able to contain a volume rather greater than the capacity of the graduated tube. Before use, the apparatus should be rinsed with liquid to be used, and after use it can be washed out with alcohol and ether in the usual way.

The advantages of this method over the trough method are obvious. The jacketed tube allows exact regulation of the temperature (which exerts considerable influence); the substitution of a mercury for a wire bridge ensures much better contact, whilst the amount of liquid necessary is less than 25 per cent. of that used in the trough method. By adapting a pump to the tap, *N*, the effect of reduced pressure could easily be studied.

THE ORGANIC CHEMISTRY LABORATORY,
UNIVERSITY COLLEGE, LONDON.

CVII.—*Titani-dihydroxymaleic Acid, and the Detection of Titanium.*

By HENRY JOHN HORSTMAN FENTON.

MANY of the properties of dihydroxymaleic acid and of dihydroxytartaric acid have already been described in previous communications to the Society. The study of these remarkable acids is still being continued, and in the present paper an account is given of some recent observations made while investigating the metallic salts of dihydroxymaleic acid.

When a warm, not too dilute, aqueous solution of a quadrivalent titanium compound is mixed, in almost any proportion, with a solution of dihydroxymaleic acid, a bulky, chocolate-coloured precipitate is produced which, in appearance and character, closely resembles cupric ferrocyanide. If the solutions are more dilute and are mixed in the cold, no precipitation takes place, but an intense orange-red colour is produced. This solution appears to be of a colloidal nature, being precipitated by boiling or by the addition of salt solutions.

The precipitate, on drying, shrinks enormously in volume, and is left in the form of extremely hard grains; these appear quite black, but yield a dark red powder when crushed. For the purpose of analysis, the following procedure was adopted.

Hydrated titanium dioxide was dissolved in concentrated sulphuric acid, diluted, filtered, and mixed while hot with an aqueous solution of dihydroxymaleic acid. The resulting precipitate was washed three or four times with hot water, and dried in a vacuum desiccator for twenty-four hours:

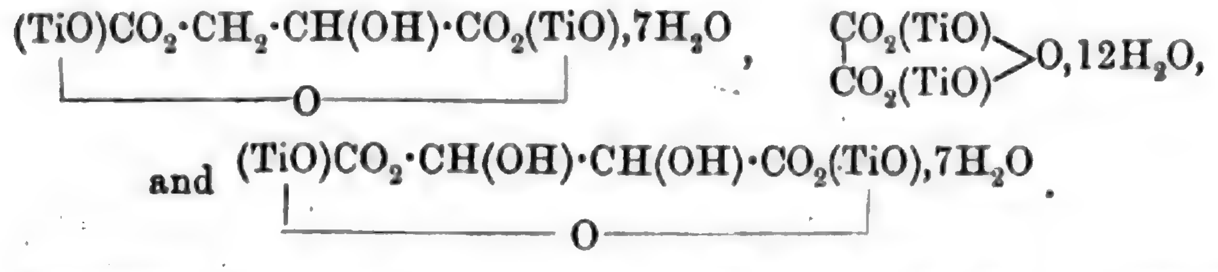
I. 0·1732 gave 0·0853 CO_2 and 0·0386 H_2O. $C = 13·43$; $H = 2·47$.
II. 0·5196 on ignition gave 0·2307 TiO_2. $TiO_2 = 44·39$.
III. 0·4219 „ „ 0·1918 TiO_2. $TiO_2 = 45·46$.
$C_4H_4O_6,2TiO_2,2\frac{1}{2}H_2O$ requires $C = 13·59$; $H = 2·54$; $TiO_2 = 45·32$ per cent.

The composition of the precipitate corresponds therefore with that of a basic salt, and resembles in this respect most other compounds of titanium with oxygen acids.

Berg, for example (*Zeitsch. anorg. Chem.*, 1897, **15**, 328), by the action of malic acid on a neutral solution of titanium tetrachloride obtained a crystalline compound having the composition

$$C_4H_6O_5,2TiO_2,6H_2O.$$

Rosenheim and Schütte (*ibid.*, 1900, **26**, 239) describe the preparation, amongst others, of the oxalate, $C_2H_2O_4,2TiO_2,11H_2O$, and the tartrate, $C_4H_6O_6,2TiO_2,6H_2O$. They regard these compounds as having the constitution:



$$\underbrace{(TiO)CO_2\cdot CH_2\cdot CH(OH)\cdot CO_2(TiO)}_{O},7H_2O, \quad \begin{matrix}CO_2(TiO)\\ | \\ CO_2(TiO)\end{matrix}\!>\!O,12H_2O,$$

$$\text{and } \underbrace{(TiO)CO_2\cdot CH(OH)\cdot CH(OH)\cdot CO_2(TiO)}_{O},7H_2O.$$

Henderson, Orr, and Whitehead (Trans., 1899, **75**, 542), by dissolving hydrated titanium dioxide in a boiling solution of potassium hydrogen tartrate, obtained a white, crystalline salt having the composition $(TiO)(C_4H_4O_6)_2,4\frac{1}{2}H_2O$. The sodium and ammonium salts were prepared similarly. The authors consider it probable that, as in tartar emetic, replacement by the (TiO) group occurs in one or more of the alcoholic hydroxyl groups. Rosenheim and Schütte state that they were unable to obtain any crystalline compounds in this way, and consider that the alkali titani-tartrates are only mixtures. It is of interest to notice, however, that they obtained another compound, by dissolving hydrated titanium dioxide in tartaric acid, which has the composition of a normal titanic tartrate, $Ti(C_4H_4O_6)_2,4H_2O$. But the compound has a remarkably high rotatory power, and this property appears to suggest a lactone linking, since a similar effect has only been observed in hydroxy-acids (compare Walden, *Ber.*, 1897, **30**, 2889).

Colour.—The compounds here referred to are all colourless, as also are those which have been obtained from mucic, citric, lactic, and apparently all other aliphatic acids. It appears very remarkable therefore that the dihydroxymaleic acid compound, now under discussion, should be so intensely coloured, and the fact may perhaps be connected with the tautomeric character of the acid (Trans., 1905, **87**, 804).

This compound when precipitated in presence of dilute sulphuric acid is, as above stated, chocolate in colour. After washing it becomes redder, like ferric hydroxide, but on treatment with strong acids it turns again darker and of a deeper purple. It is remarkably stable towards acids, being scarcely changed by cold concentrated sulphuric acid or hot concentrated hydrochloric acid. Hydrofluoric acid, however, at once decomposes it, and the resulting solution then gives the reactions of dihydroxymaleic acid. Cold alkaline hydroxides or carbonates change it at once into bright orange-yellow salts, which are nearly insoluble in water. These salts, when treated with acids, regenerate the original chocolate-coloured substance. When boiled with alkalis in excess, the compounds are decomposed, yielding a salt of dihydroxymaleic acid. The original compound also undergoes a certain amount of hydrolytic decomposition when repeatedly washed with large quantities of boiling water. This fact is indicated by the increased content of titanium, but the appearance of the compound is scarcely altered.

The original compound dissolves sufficiently in cold water to give a yellowish-red solution. Acids change this to pinkish-brown, and alkalis to lemon-yellow. The colour changes are quite sharp, and the tints nearly resemble those given by methyl-orange, but are less intense.

In terms of Ostwald's simpler explanation, one would say therefore that the ion is yellow and the undissociated compound pinkish-brown, but the changes could no doubt be referred to a difference in constitution.

Without additional evidence there is not much object in making conjectures with regard to the constitution of this substance. The fact that it behaves as an acid, appears to exclude the simple anhydride-like constitution which Rosenheim and Schütte assign to the oxalic, malic, and tartaric acid compounds of titanium.

That replacement has occurred, in part at any rate, in the alcoholic hydroxyl groups is also indicated by the following observations. A solution of dihydroxymaleic dimethyl ester, in dry ether or alcohol, gives an intense orange-red colour with dry titanium tetrachloride, dissolved in the same solvents. This colour is quite similar to that obtained from cold aqueous solutions as mentioned below. Further, the diacetyl acid (Trans., 1896, **69**, 551) gives no colour with titanium compounds in aqueous solution.

Detection of Titanium.—When cold aqueous solutions of dihydroxymaleic acid and quadrivalent titanium compounds are mixed in the cold, intensely-coloured solutions are obtained, the shade of colour depending on the dilution. A solution containing one part of titanium in 15,000 gives an intense orange-red colour, and one part in 150,000 is coloured bright lemon-yellow. Beyond this the colour becomes paler, but is a very distinct straw-yellow at a dilution of one in a million. By viewing the solution through a column of 20 or 30 centimetres in length, it is quite easy to observe the colour produced by one part of titanium in about five millions.

Rough comparisons made under similar conditions with the well-known hydrogen dioxide test indicate that the dihydroxymaleic acid reaction is from fifteen to twenty times as delicate. For the quantitative estimation of titanium by the colorimetric process, the latter will doubtless be found to be advantageous, not only because of its greater sensitiveness, but also on account of the more marked variation of tint with dilution.

The test has the further advantage that it is not given by vanadium. Molybdates and uranyl salts give red or brown colours, but these are easily distinguished, since they are destroyed by acids, the former on heating and the latter in the cold. Tungstic acid also gives a brown colour, but this is almost immediately changed to blue; vanadic compounds yield only a blue solution. Negative results are given by thorium, cerium, zirconium, silicon, and tin.

Iron in the ferric state interferes with the test in so far that it destroys the reagent (Trans., 1902, **81**, 426). If only traces of iron are present, it suffices to add an excess of the reagent; otherwise it is necessary to reduce the iron to the ferrous condition by means of sulphurous acid.

Influence of Fluorides.—The colour-reaction here described is entirely prevented by the presence of fluorides, and the chocolate-coloured precipitate, described above, dissolves completely in warm hydrofluoric acid, yielding a colourless solution. Fluorides, as is well known, have a similar influence in preventing the colour reaction of titanium with hydrogen dioxide, and Steiger (*J. Amer. Chem. Soc.*, 1908, **30**, 219) has devised a colorimetric method, depending on this circumstance, for the estimation of small quantities of fluorine. For the application of his method, it is probable that the use of dihydroxymaleic acid may be found to be preferable to that of hydrogen dioxide for the reasons indicated above.

It would appear therefore that both these tests are to be regarded as distinctive of titanium ions, and that the inhibiting effect of fluorides is to be ascribed to the withdrawal of these to form the complex TiF_6 ions.

A strong solution of potassium titanifluoride gives a yellowish-brown solution on the addition of dihydroxymaleic acid; on dilution, the colour quickly changes to straw-yellow. Here there is presumably equilibrium in the sense:

$$6F' + \overset{\cdot\cdot\cdot\cdot}{Ti} \rightleftarrows (TiF_6)''.$$

Addition of a solution of potassium fluoride here again quickly bleaches the colour.

The existence of hydrofluotitanic acid in aqueous solution was indicated by the experiments of Kowalewsky (*Zeitsch. anorg. Chem.*, 1900, **25**, 193), who showed that the electric conductivity of a solution of hydrofluoric acid is increased when titanium dioxide is dissolved in it, hydrofluotitanic acid being relatively a strong acid.

Consequently one would expect that the addition of strong mineral acids would, by "suppressing" the F', have a retrogade influence on the change above mentioned. The following preliminary experiments appear to favour this view.

A solution of titanium dioxide in sulphuric acid, containing 0·02128 TiO_2 per c.c., was run into known quantities of pure potassium fluoride dissolved in very small quantities of water, dihydroxymaleic acid being added as indicator. If the solutions are sufficiently concentrated, the end point is quite well defined. A reddish-brown spot is produced on addition of each drop of the titanium solution, which is immediately bleached on mixing with the surrounding liquid; the end is characterised by the first appearance of a permanent, pale straw-yellow colour, which on further additions of the titanium solution is changed to a permanent reddish-brown:

I. 0·9537 potassium fluoride, mixed with dilute sulphuric acid in excess, required 9·5 c.c. TiO_2 solution (= 0·2021 gram TiO_2).

Theory for 6KF: Ti = 10·3 c.c. (= 0·2192 gram TiO_2).

II. 1·4315 potassium fluoride, under similar conditions, required 14·5 c.c. TiO_2 solution (= 0·3085 gram TiO_2).

Theory, 15·4 c.c. (= 0·3290 gram TiO_2).

III. 1·2501 potassium fluoride, mixed with excess of potassium acetate and a little acetic acid, required 13·1 c.c. TiO_2 solution (= 0·2787 gram TiO_2).

Theory, 13·5 c.c. (= 2873 gram TiO_2).

These experiments were carried out in glass dishes coated with paraffin wax.

It would appear that this method would serve well for the approximate volumetric estimation of fluorides. The solutions would have to be fairly concentrated in order to ensure a sufficiently sharp end-point, and it would probably be preferable to standardise the titanium solutions by means of a pure fluoride under similar conditions of dilution, &c. Experiments will shortly be carried out in order to test this suggestion, and it is possible that the reaction may also be of theoretical interest in studying the conditions affecting the equilibrium between fluorine and titanium which has been already referred to.

Behaviour of Dihydroxytartaric Acid.—Solutions of titanium compounds when mixed in aqueous solution with dihydroxytartaric acid in the cold remain quite colourless. On warming to about 70° or 80°, an orange-red precipitate separates, which appears to be identical with the compound which is given by dihydroxymaleic acid. When washed and decomposed with hydrofluoric acid, it gives, in fact, the reactions of dihydroxymaleic acid.

No oxygen is evolved during this change, and it would appear therefore that the quadrivalent titanium must become peroxidised:

$$C_4H_6O_8 + TiO_2 = C_4H_4O_6 + TiO_3 + H_2O.$$

Further evidence in this direction is afforded by the fact that the filtrate, after removal of the precipitate, is invariably coloured a deep orange, even although considerable excess of titanium has been added, whereas in the case of dihydroxymaleic acid the filtrate under similar conditions is practically colourless.

This change appears therefore to afford another example of the remarkable oxidising capability of dihydroxytartaric acid (compare Trans., 1898, **73**, 80).

CVIII.—*The Triazo-group. Part III. Bistriazo-derivatives of Ethane and of Acetic Ester.*

By Martin Onslow Forster, Hans Eduard Fierz, and Walter Philip Joshua.

The facility with which the triazo-group may be introduced into typical organic molecules of simple structure by interaction of sodium azide and the appropriate halogen derivative led us to consider the possibility of studying representative bistriazo-derivatives. Hitherto, the only compounds which contain two triazo-groups replacing hydrogen in elementary hydrocarbon types have been the para-bistriazobenzene of Griess (*Ber.*, 1888, **21**, 1559; compare also Silberrad and Smart, Trans., 1906, **89**, 170), and meta-bistriazobenzene (Forster and Fierz, Trans., 1907, **91**, 1953). Accordingly, we have prepared bistriazo-derivatives from ethylene dichloride, ethylidene dichloride, and dichloroacetic ester, and it appears to us necessary that a note of warning should be uttered against manipulating the products; our hazardous experiences have led us to abandon the investigation of those bistriazo-derivatives in which both triazo-groups are attached to one carbon atom.

Dimroth and Wislicenus (*Ber.*, 1905, **38**, 1573) were the first to prepare a triazo-hydrocarbon of the aliphatic series, and described the simplest of these, methylazoimide, as arising from the action of methyl sulphate on an aqueous solution of sodium azide. By heating ethylene dichloride with sodium azide in dilute alcohol, we have obtained symmetrical bistriazoethane in the form of a colourless, refractive liquid, which has the odour of chloroform, and boils at 53° under 9 mm. pressure. The readiness with which the substance is converted into ethylenediamine by reduction tempted us to prepare unsymmetrical bistriazoethane in the hope of arriving at ethylidenediamine, but for reasons appearing below the experiment will not be pursued, and the expectation of obtaining diaminoacetic ester must remain also unfulfilled.

Conspicuous among the developments of Grignard's reaction have been the experiments of Dimroth with alkyl and aryl azoimides (*Ber.*, 1905, **38**, 670, 2328; 1906, **39**, 3905; 1907, **40**, 2390), the intermediate magnesium derivatives from which yield diazoamino-compounds when treated with water. In this manner, Dimroth obtained diazoaminobenzene from phenylazoimide and magnesium phenyl bromide, subsequently preparing numerous aliphatic-aromatic diazoamino-compounds, or triazenes, by varying both the azoimide and the Grignard agent; the most remarkable member of the series, dimethyltriazene, or diazoaminomethane, arises from methylazoimide and magnesium methyl iodide (Dimroth, *Ber.*, 1906, **39**, 3905). Applying this reaction to symmetrical bistriazoethane, we have prepared the compound,

$$C_6H_5\cdot NH\cdot N:N\cdot CH_2\cdot CH_2\cdot N:N\cdot NH\cdot C_6H_5,$$

which has the properties of a mixed diazoamino-derivative, yielding two-thirds of its nitrogen when treated with cold dilute acids; the appearance of aniline unmixed with diazonium salt as a result of this decomposition would appear to justify the above representation (compare Dimroth, Eble, and Gruhl, *Ber.*, 1907, **40**, 2390).

EXPERIMENTAL.

1 : 2-*Bistriazoethane*, $N_3\cdot CH_2\cdot CH_2\cdot N_3$.

Fifty grams of ethylene dichloride and 80 c.c. of alcohol were heated under reflux during four days with 65 grams of sodium azide in 200 c.c. of water. The liquid having been diluted with 500 c.c. of water was extracted four times with ether, and the latter, after desiccation with calcium chloride, was distilled under ordinary pressure, carrying with it 10 grams of ethylene dichloride. The residue was then fractionated three times under 9 mm. pressure, 20 grams of a colourless, refractive oil being finally obtained, distilling at a constant temperature of 53°. On attempting to estimate nitrogen in the ordinary way, a violent explosion occurred, even when a few drops of the compound, largely diluted with copper oxide, were slowly vaporised; we are indebted to Mr. Richmond, however, for analyses of this material and of bistriazoacetic ester by the method devised by him for dealing with triazo-derivatives (*Analyst*, 1908, **33**, 180):

0·1104 gave 46·7 c.c. of nitrogen at 19° and 754 mm., along with 0·0335 gram of ammonia. N = 49·9 as gas, 25·0 as NH_3; total, 74·9.

$C_2H_4N_6$ requires N = 75·0 per cent.

Bistriazoethane has a sweet taste and the odour of chloroform, the vapour stimulating salivation and producing slight palpitation of the heart. Its specific gravity is 1·178 compared with water at 19°, and it is readily volatile in steam. When thrown on a hot plate, it explodes, and its behaviour with concentrated sulphuric acid is treacherous, evolution of gas taking place quite smoothly, although very briskly if the materials are mixed immediately, whilst a mild explosion occurs if action is delayed; on one occasion, however, the acid was added to a few drops of the azide on a watch-glass without the customary evolution of gas taking place, when suddenly a terrific detonation occurred, and the watch-glass simply vanished. Alcoholic alkali eliminates hydrazoic acid from bistriazoethane very slowly, without liberation of nitrogen gas.

Reduction to Ethylenediamine.—Alcoholic ammonium sulphide reduces the substance immediately, torrents of nitrogen being set free. On adding a solution of stannous chloride in hydrochloric acid to the bistriazo-compound dissolved in alcohol, steady evolution of nitrogen occurs, approximately two-thirds of the total content:

0·1853 gave 76·0 c.c. of nitrogen at 16° and 751 mm. N = 47·9.

$C_2H_4N_6$ requires 2/3N = 50·0 per cent.

In order to identify the product of reduction, 10 grams were treated with a solution containing 20 grams of tin, when the oil quickly disappeared, yielding 25 grams of the tin double salt; 5 grams of this material were shaken with alkali and benzoyl chloride, yielding the dibenzoyl derivative of ethylenediamine, the remainder being converted into the hydrochloride of that base, from which the platinichloride was prepared:

0·6263 gave 0·2584 Pt. Pt = 41·26.

$C_2H_8N_2,H_2PtCl_6$ requires Pt = 41·70 per cent.

The base was further identified by the picrate, and the absence of hydrazine was established.

Action of Magnesium Phenyl Bromide on Bistriazoethane.

Twenty grams of bromobenzene in 40 c.c. of dry ether having been converted into magnesium phenyl bromide with 3·2 grams of the metal, the solution was mixed with 7 grams of bistriazoethane in 20 c.c. of ether without external cooling, when a somewhat vigorous action took place. After an interval of ten minutes, a mixture of crushed ice and concentrated ammonium chloride was added, the diazoamino-compound being extracted without delay by shaking with successive quantities of ether, amounting to about 400 c.c. Contact with undissolved magnesium was found to have a catalytic effect on the product, as in the case of the substances described by Dimroth. The solution having been dried by calcium chloride, ether was evaporated, and petroleum added to the residue, when 12 grams of crystalline material were obtained; the mother liquor deposited on evaporation an oil which had the odour of phenylcarbylamine.

The compound being very sparingly soluble in boiling petroleum, it was recrystallised from this medium (b. p. 80—100°), about two litres being required to dissolve 8 grams; the solution deposited lustrous, square plates having a faint brown tinge, and melting with vigorous gas evolution at 128°:

0·1440 gave 0·3311 CO_2 and 0·0801 H_2O. C = 62·71; H = 6·22.
0·0824 „ 22·3 c.c. of nitrogen at 20° and 760 mm. N = 31·69.
$C_{14}H_{16}N_6$ requires C = 62·69; H = 5·97; N = 31·34 per cent.

The diazoamino-compound is sparingly soluble in ether, chloroform, benzene, and alcohol, dissolving with moderate readiness in the two last-named solvents when heated.

Decomposition with Dilute Acids.—The compound is remarkably sensitive towards dilute acids, even acetic acid liberating nitrogen immediately; when treated with 8 per cent. hydrochloric acid,

0·2868 gave 51·8 c.c. of nitrogen at 16° and 756 mm. N = 21·22.
$C_{14}H_{16}N_6$ requires 2/3N = 20·89 per cent.

The principal product of this decomposition was found to be aniline, and ethylene dichloride could not be recognised. An experiment in which the acid liquid was added immediately to an alkaline solution of β-naphthol indicated the formation of diazonium salt in negligible amount.

Attempt to Prepare 1 : 1-*Bistriazoethane*, $CH_3 \cdot CH(N_3)_2$.

Fifty grams of ethylidene dichloride and 100 c.c. of alcohol were heated under reflux during sixty hours with 70 grams of sodium azide in 200 c.c. of water; the steam distillate having been extracted with ether, this was dried with calcium chloride and fractionated with a long rod-and-disk column on the water-bath, almost everything passing over between 40° and 50°, when there remained 3 c.c. of liquid residue. This was successfully distilled at 38° under 14 mm. pressure, leaving only one drop of a yellow oil, but on admitting air to the apparatus a disastrous explosion occurred, apparently starting in the Brühl jar; by a curious chance, the thermometers in the distilling flask and in the surrounding water-bath escaped fracture, although the thick glass receiver was transformed into coarse powder, and the Liebig's condenser disappeared.

Our experience of the purified substance lasted only a few minutes, during which we were able to recognise it as a colourless, refractive liquid which, previous to distillation, had the odour of chloroform.

Bistriazoacetic Ester, $CH(N_3)_2 \cdot CO_2 \cdot C_2H_5$.

Eighty-five grams of dichloroacetic ester mixed with the same quantity of alcohol were heated under reflux during five hours with

75 grams of sodium azide in 200 c.c. of water, steady liberation of hydrazoic acid being noticed throughout the experiment. The product of steam distillation was extracted with ether, and, after removing the solvent, fractionated under 2 mm. pressure; the major portion distilled below 70°, but 13·5 grams of a colourless liquid were obtained, free from chlorine, and boiling steadily at 70—72°. An attempt to estimate nitrogen by the ordinary method led to a violent explosion. Mr. Richmond found, however, that

0·1764 gave 49·55 c.c. of nitrogen at 16·5° and 757 mm., along with 0·03538 gram of ammonia. N = 32·98 as gas, 16·52 as NH_3; total, 49·50.

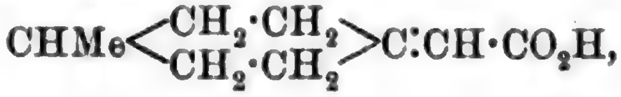
$C_4H_6O_2N_6$ requires N = 49·41 per cent.

Bistriazoacetic ester is a colourless, odourless liquid, having specific gravity 1·222 compared with water at 18°. When mixed with concentrated sulphuric acid, torrents of gas are liberated, and action is liable to be explosive; with aqueous potassium hydroxide, the substance behaves like triazoacetic ester, evolution of gas being sluggish at first, and becoming brisk only on vigorous shaking. Attempts to prepare bistriazoacetic acid were unsuccessful, owing to the readiness with which hydrazoic acid is eliminated, a feature which doubtless explains the highly explosive character of the substance as compared with triazoacetic ester; even cold alcoholic ammonia brings about this change, so that transformation into bistriazoacetamide was not realised. No conclusions could be drawn regarding the action of stannous chloride, which liberated only 8·6 per cent. of nitrogen, and the substance was considered too dangerous for further investigation.

This opportunity may be taken to emphasise the value of Messrs. Pilkingtons' wired glass for screens to protect the operator during distillation under reduced pressure. It would be advantageous also if the Brühl jar could be made of this material, as the thickness of the glass from which these vessels are usually constructed renders them very dangerous objects in an explosion as distinguished from a collapse.

ROYAL COLLEGE OF SCIENCE, LONDON,
SOUTH KENSINGTON, S.W.

CIX.—*Experiments on the Synthesis of* 1-*Methyl*cyclo*hexylidene*-4-*acetic Acid*,

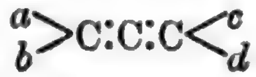


$$\mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}{>}\mathrm{C{:}CH{\cdot}CO_2H},$$

Part I.

By WILLIAM HENRY PERKIN, jun., and WILLIAM JACKSON POPE.

VAN'T HOFF has pointed out that the presence of an asymmetric atom is conceivably not the only cause from which optical activity can arise; a substance containing an asymmetric carbon atom exhibits optical activity in solution, because the presence of this peculiarity of constitution imparts an enantiomorphous configuration to the molecule. It is, however, possible to devise space formulæ which are enantiomorphous, but which contain no asymmetric atom; the substances thus represented would be expected to exhibit optical activity in solution. Thus van't Hoff notes (*The Arrangement of Atoms in Space*, 1898, 103) that allene derivatives of the type

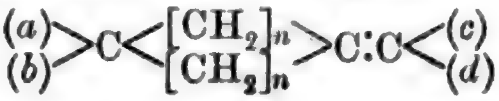


$$\begin{matrix}a\\ b\end{matrix}{>}\mathrm{C{:}C{:}C}{<}\begin{matrix}c\\ d\end{matrix}$$

should exist in two enantiomorphously related, and hence optically active, forms.

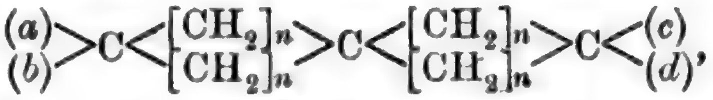
Compounds which presumably possess enantiomorphous configurations, such as are described above, are already known, as, for instance, the symmetrical dimethylallene, CHMe:C:CHMe, but being synthetic products they naturally do not exhibit optical activity.

In order to obtain experimental information concerning the new kind of stereoisomerism thus indicated, we endeavoured, but without success, to prepare allene derivatives of the type mentioned, and of such constitutions that the ordinary methods of resolving externally compensated substances could be applied to them. We next turned our attention to the synthesis of compounds belonging to the types



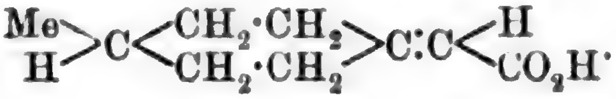
$$\begin{matrix}(a)\\ (b)\end{matrix}{>}\mathrm{C}{<}\begin{matrix}[\mathrm{CH_2}]_n\\ [\mathrm{CH_2}]_n\end{matrix}{>}\mathrm{C{:}C}{<}\begin{matrix}(c)\\ (d)\end{matrix}$$

and



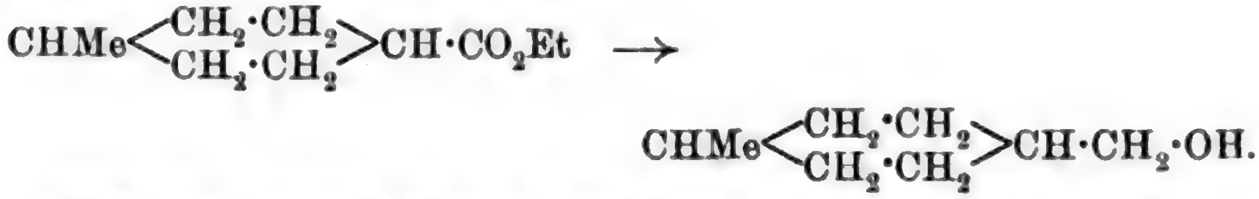
$$\begin{matrix}(a)\\ (b)\end{matrix}{>}\mathrm{C}{<}\begin{matrix}[\mathrm{CH_2}]_n\\ [\mathrm{CH_2}]_n\end{matrix}{>}\mathrm{C}{<}\begin{matrix}[\mathrm{CH_2}]_n\\ [\mathrm{CH_2}]_n\end{matrix}{>}\mathrm{C}{<}\begin{matrix}(c)\\ (d)\end{matrix},$$

which contain symmetrical closed rings in the place of one or both of the double linkings in allene, and must therefore also exhibit enantiomorphism, and we selected for our purpose the synthesis of 1-*methyl*cyclo*hexylidene*-4-*acetic acid*,



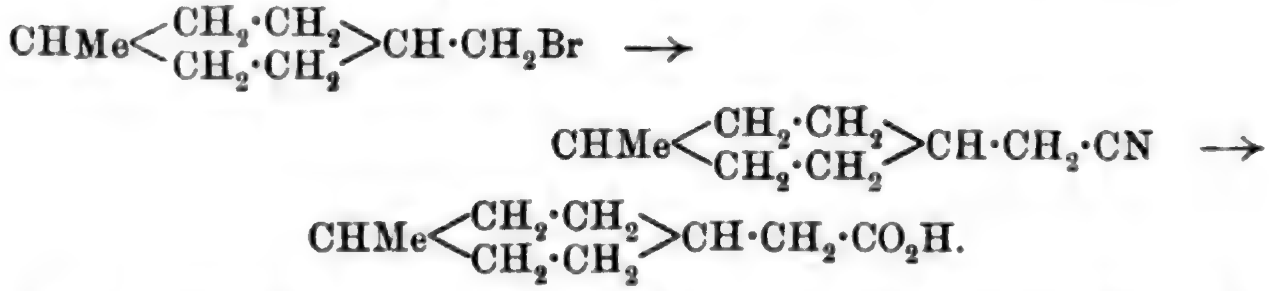
$$\begin{matrix}\mathrm{Me}\\ \mathrm{H}\end{matrix}{>}\mathrm{C}{<}\begin{matrix}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}{>}\mathrm{C{:}C}{<}\begin{matrix}\mathrm{H}\\ \mathrm{CO_2H}\end{matrix}.$$

The starting point in this synthesis was 1-*methyl*cyclo*hexylcarbinol*, which was prepared in considerable quantities from ethyl 1-methyl*cyclo*hexane-4-carboxylate (Trans., 1905, **87**, 644) by reduction with sodium and alcohol,



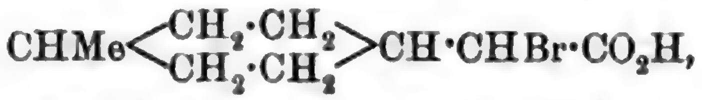
$$\mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2\cdot CH_2}\\\mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{CH\cdot CO_2Et}\ \longrightarrow\ \mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2\cdot CH_2}\\\mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{CH\cdot CH_2\cdot OH}.$$

When this alcohol is heated with fuming hydrobromic acid, it yields 1-*methyl*cyclo*hexylcarbinyl bromide*, and this is converted by the action of potassium cyanide into the corresponding nitrile, which, on hydrolysis, yields 1-*methyl*cyclo*hexyl*-4-*acetic acid*:



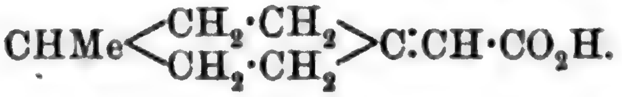
$$\mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2\cdot CH_2}\\\mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{CH\cdot CH_2Br}\ \longrightarrow\ \mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2\cdot CH_2}\\\mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{CH\cdot CH_2\cdot CN}\ \longrightarrow\ \mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2\cdot CH_2}\\\mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{CH\cdot CH_2\cdot CO_2H}.$$

The chloride of this acid behaves in the usual manner when it is heated with bromine, and the product is readily decomposed by formic acid with formation of *a-bromo*-1-*methyl*cyclo*hexyl*-4-*acetic acid*,



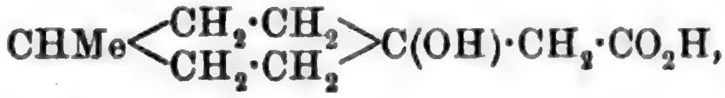
$$\mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2\cdot CH_2}\\\mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{CH\cdot CHBr\cdot CO_2H},$$

which crystallises well and melts at 78°. When the ester of the acid is digested with diethylaniline, hydrogen bromide is eliminated, and an unsaturated ester is formed, and this, on hydrolysis, yields an acid which crystallises from formic acid in glistening plates, softens at 63°, and melts at 70°. The analysis of this acid gave results agreeing with the formula $C_9H_{14}O_2$, and this formula was confirmed by the analysis of the ester and other derivatives. Since the alkaline solution of the acid instantly decolorised permanganate, there seemed to be no other alternative than to conclude that it had been produced normally, and was, in fact, 1-*methyl*cyclo*hexylidene*-4-*acetic acid*,



$$\mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2\cdot CH_2}\\\mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{C{:}CH\cdot CO_2H}.$$

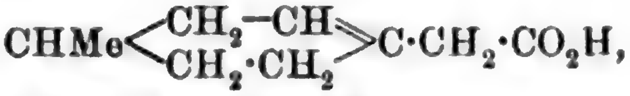
While these experiments were in progress, W. Markwald and R. Meth (*Ber.*, 1906, **39**, 1171) published an account of an investigation which they had made with the same object as we had in view, namely, that of synthesising 1-methyl*cyclo*hexylidene-4-acetic acid and then resolving it into its active modifications. Their method of synthesising this acid was, however, quite different from ours, and was as follows: 4-Methyl*cyclo*hexanone was treated with ethyl bromoacetate and magnesium and the product hydrolysed, when the two stereoisomeric modifications of 4-hydroxy-1-methyl*cyclo*hexyl-4-acetic acid,



$$\mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2{\cdot}CH_2}\\\mathrm{CH_2{\cdot}CH_2}\end{matrix}{>}\mathrm{C(OH){\cdot}CH_2{\cdot}CO_2H},$$

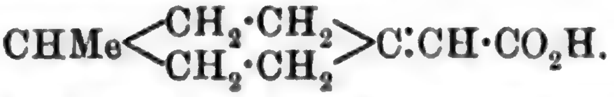
were obtained, both of which are decomposed by boiling dilute sulphuric acid with elimination of water and formation of an unsaturated acid, $C_9H_{14}O_2$, which melts at 41°.

A glance at the formula of the hydroxy-acid shows at once that the elimination of water may take place in two directions, and that the resulting unsaturated acid may be either 1-methyl-Δ^3-*cyclo*hexene-4-acetic acid,



$$\mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2{-}CH}\\\mathrm{CH_2{\cdot}CH_2}\end{matrix}{\geqslant}\mathrm{C{\cdot}CH_2{\cdot}CO_2H},$$

or 1-methyl*cyclo*hexylidene-4-acetic acid,



$$\mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2{\cdot}CH_2}\\\mathrm{CH_2{\cdot}CH_2}\end{matrix}{>}\mathrm{C{:}CH{\cdot}CO_2H}.$$

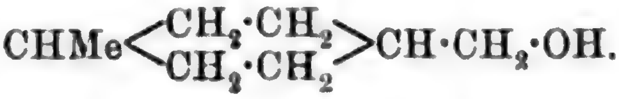
Markwald and Meth are of opinion that their unsaturated acid is to be regarded as having the latter constitution, but we, on the other hand, consider it probable that it contains the double linking in the ring, and is, in fact, 1-methyl-Δ^3-*cyclo*hexene-4-acetic acid.

In reply to this criticism, Markwald and Meth (*Ber*., 1906, **39**, 2404) have published further evidence in support of their view, and Wallach (*Annalen*, 1907, **313**, 311) has also investigated the subject, and is of opinion that the acid of melting point 41° is 1-methyl*cyclo*hexylidene-4-acetic acid. It is unfortunate that we have not yet been able to prepare our unsaturated acid free from small quantities of 1-methyl*cyclo*hexyl-4-acetic acid. The ester of this latter acid is apparently produced in small quantities as the result of a secondary reaction during the elimination of hydrogen bromide from ethyl α-bromo-1-methyl*cyclo*hexyl-4-acetate by means of diethylaniline, and its presence was first discovered during a series of experiments on the oxidation of the unsaturated acid by means of ozone.

It follows from this that the melting point which we have given for our unsaturated acid can only be approximately correct, and must therefore be accepted with reserve. On the other hand, the results of a long and interesting series of experiments which are in progress seem to show that, in spite of all the evidence to the contrary, the unsaturated acid of melting point 41°, prepared by Markwald and Meth, is not 1-methyl*cyclo*hexylidene-4-acetic acid.

The experimental investigation of this matter has proved to be most complex and difficult, and, as the investigation may not be completed for a considerable time, we have thought it best to publish now the details of those experiments of which a brief account was given in our preliminary communication (Proc., 1906, **22**, 107).

1-*Methyl*cyclo*hexyl*-4-*carbinol*,



$$CHMe<\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CH_2\cdot CH_2}>CH\cdot CH_2\cdot OH.$$

The process used in the preparation of this carbinol is similar to that employed by Bouveault and Blanc (*Compt. rend.*, 1903, **136**, 1676; **137**, 60) in their experiments on the conversion of *cyclo*hexanecarboxylic ester into *cyclo*hexylcarbinol. Sodium (30 grams), in pieces about the size of a marble, is placed in a 2-litre flask, connected with a long condenser, and heated in an oil-bath at 80°.

1-Methyl*cyclo*hexane-4-carboxylic ester (30 grams), dissolved in alcohol (150 c.c.), is then added in a thin stream down the condenser, the decomposition being allowed to proceed as vigorously as possible.

When the action slakens, the temperature of the oil-bath is raised to 130°, and small quantities of alcohol added until the sodium has dissolved. The product is diluted with water (3 vols.) and extracted three times with ether, the ethereal solution is washed several times with water, dried over anhydrous sodium sulphate, evaporated, and the residual oil purified by distillation under ordinary pressure. During the first distillation almost the whole quantity passes over at 190—200°, very little oil of higher boiling point remaining in the flask, and, on repeating the operation, the substance boils constantly at 197—198° (768 mm.):

0·1726 gave 0·4734 CO_2 and 0·1886 H_2O. C = 74·8; H = 12·2.
0·1382 „ 0·3790 CO_2 „ 0·1539 H_2O. C = 74·8; H = 12·4.
$C_8H_{16}O$ requires C = 75·0; H = 12·4 per cent.

1-*Methyl*cyclo*hexyl*-4-*carbinol* has an odour of *iso*amyl alcohol and at the same time of peppermint. The yield of alcohol obtained by the above process is 20—25 grams from 60 grams of 1-methyl*cyclo*hexane-4-carboxylic ester, and the alkaline solution, from which the alcohol has been extracted with ether, yields on concentration and precipitation with hydrochloric acid the unchanged 1-methyl*cyclo*hexane-4-carboxylic acid, which is collected and used in a subsequent operation.

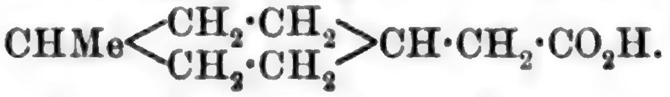
1-*Methyl*cyclo*hexyl*-4-*carbinyl Bromide.*—1-Methyl*cyclo*hexyl-4-carbinol dissolves in twice its volume of a solution of hydrogen bromide in glacial acetic acid (saturated at 0°) with very little rise of temperature, and if heated for two hours at 100° and then for one hour at 120° the liquid separates into two layers.

The whole is diluted with water, extracted with ether, the ethereal solution well washed with water, dried, and evaporated. The residual bromide distils at 135—137° under 150 mm. pressure, the yield being almost quantitative:

0·5274 gave 0·5136 AgBr. Br = 41·5.
$C_8H_{15}Br$ requires Br = 41·8 per cent.

1-*Methyl*cyclo*hexyl-4-carbinyl bromide* is a very stable substance, which may be distilled in small quantities under the ordinary pressure with only slight decomposition. It has a pungent and rather aromatic odour, which somewhat resembles that of trimethylene bromide.

1-*Methyl*cyclo*hexyl-4-acetic Acid*,



$$CHMe{<}\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}{>}CH\cdot CH_2\cdot CO_2H.$$

Three methods have been employed in the preparation of this acid.

Method I. *The Hydrolysis of* 1-*Methyl*cyclo*hexyl-4 carbinyl Cyanide*.—This process was found to be very laborious on account of the fact that 1-methyl*cyclo*hexyl-4-carbinyl bromide is not readily converted into the cyanide by treatment with potassium cyanide.

After a long series of comparative experiments, carried out under very varied conditions, the following process, which still leaves much to be desired, seemed to yield the best results. The bromide (10 grams) is heated in a sealed tube with pure potassium cyanide (Kahlbaum, 10 grams) and 70 per cent. alcohol (30 c.c.) for two hours at 120°, the tube is then allowed to cool, well shaken, and heated at 150° for three hours. The product, which smells of ammonia and, owing to the separation of azulmic acid, is very dark coloured, is diluted with water, extracted with ether, the ethereal solution washed with water until free from alcohol, and evaporated.

The residue, which has a pungent odour of a cyanide and consists of 1-methyl*cyclo*hexyl-4-carbinyl cyanide and a considerable quantity of regenerated 1-methyl*cyclo*hexyl-4-carbinol, is mixed with an equal volume of acetic-hydrobromic acid (saturated at 0°) and heated in a sealed tube at 120° for two hours. The product contains crystals of ammonium bromide, and is diluted with water, extracted with ether, the ethereal solution washed several times with water in order to remove as much acetic acid as possible, and then extracted with dilute potassium hydroxide. After drying over calcium chloride, the ethereal solution yields, on evaporation, methyl*cyclo*hexylcarbinyl bromide, which is distilled and used in a subsequent operation. The potassium hydroxide solution is again extracted with ether, heated on the water-bath until free from ether, cooled with ice, and acidified, when about 1·5—2 grams of a yellow, crystalline acid separates.

This is collected, washed well, dissolved in sodium carbonate, the solution digested with animal charcoal, filtered and acidified, and the colourless, crystalline acid purified by recrystallisation from formic acid, from which it separates in satiny plates which melt at 73—74°.

Method II. *The Action of Magnesium and Carbon Dioxide on* 1-*Methyl*cyclo*hexyl-4-carbinyl Bromide*.—Magnesium (8 grams) is suspended in ether and rendered active by treatment with a little methyl iodide; the ether is then decanted and replaced by an ethereal solution of methyl*cyclo*hexylcarbinyl bromide (30 grams), when a rather vigorous action takes place, which, however, soon slackens. After heating for one hour on the water-bath, carefully-dried carbon dioxide is passed for two hours, the whole decomposed by dilute hydrochloric acid, and extracted with ether.

The ethereal extract is shaken with dilute potassium hydroxide, and the alkaline solution, after heating on the water-bath until free from ether, cooled and acidified, when a pale yellow, crystalline precipitate (3 grams) is obtained, which, after crystallisation from formic acid, melts at 73—74°. As the amount of acid obtained in this way was so small, another experiment was made, using magnesium which has been rendered active by heating with iodine under the conditions recommended by Baeyer (*Ber.*, 1905, **38**, 2759), but the yield was not much better.

The disadvantage in the use of magnesium lies in the fact that excess has to be employed, and, when the product is subsequently treated with hydrochloric acid, a good deal of the unchanged bromide becomes reduced and thus very valuable material is lost. It was for this reason that this method was abandoned.

Method III. *The Reduction of β-Bromo*-1-*methyl*cyclo*hexyl*-4-*acetic Acid* (p. 1082).*—This method, which is probably the most satisfactory for the preparation of methyl*cyclo*hexylacetic acid, is carried out in the following way. β-Bromomethyl*cyclo*hexylacetic acid is dissolved in cold alcohol, mixed with acetic acid and a few drops of hydrochloric acid, magnesium turnings are then added, and the whole well agitated, care being taken that the temperature does not rise above 35°. As soon as the magnesium has dissolved, the product is distilled in steam, and the distillate, which contains besides methyl*cyclo*hexylacetic acid considerable quantities of methyl*cyclo*hexylideneacetic acid (m. p. 41° of Markwald and Meth, p. 1077), is then neutralised with sodium carbonate and oxidised with potassium permanganate (1 per cent.) until the pink colour remains. The filtrate and washings of the manganese precipitate are evaporated to a small bulk and acidified, when a colourless acid separates which, after crystallisation from formic acid, melts at 73° and consists of pure methyl*cyclo*hexylacetic acid. The acid prepared by each of the above methods was analysed with the following results:

---

* Wallach (*Annalen*, 1907, **353**, 313) has lately prepared 1-methyl*cyclo*hexyl-4-acetic-acid from ethyl β-hydroxy-1-methyl*cyclo*hexyl-4-acetate by treatment with acetic-hydrobromic acid and subsequent reduction with zinc dust. The melting point (63—65°) which he gives is, however, too low.

I. 0·1442 gave 0·3674 CO_2 and 0·1332 H_2O. C = 69·4; H = 10·3.
II. 0·1589 „ 0·4031 CO_2 „ 0·1471 H_2O. C = 69·1; H = 10·3.
III. 0·1115 „ 0·2826 CO_2 „ 0·1032 H_2O. C = 69·1; H = 10·3.
$C_9H_{16}O_2$ requires C = 69·2; H = 10·3 per cent.

1-*Methyl*cyclo*hexyl*-4-*acetic acid* melts at 73—74°, and is readily soluble in most organic solvents, but almost insoluble in cold water.

It separates from dilute formic acid in colourless, glistening plates with a satiny lustre.

The *silver* salt, $C_9H_{15}O_2Ag$, obtained by adding silver nitrate to a slightly alkaline solution of the ammonium salt, is a white, caseous precipitate, which rapidly becomes crystalline. It was well washed and dried over sulphuric acid:

0·2665 gave 0·4000 CO_2 and 0·1363 H_2O. C = 41·3; H = 5·7.
0·3738 „ 0·1546 Ag. Ag = 41·3.
$C_9H_{15}O_2Ag$ requires C = 41·1; H = 5·7; Ag = 41·1 per cent.

a-Bromo-1-*methyl*cyclo*hexyl*-4-*acetic Acid.*—The bromination of methyl*cyclo*hexylacetic acid was carried out under the following conditions. The acid (3·5 grams) was mixed with phosphorus pentachloride (5 grams) in a tube, and, when the formation of the acid chloride was complete, bromine (4 grams) was added, the tube sealed, and heated in boiling water for ten hours. The product, which was only slightly coloured, was mixed with three volumes of formic acid (sp. gr. 1·22) and heated for about an hour on the water-bath, when it was noticed that the liquid had separated into two layers. Since no crystallisation * took place after standing for twenty-four hours, the bromo-acid was precipitated by adding water, the gum which separated was kneaded with cold water until it had solidified, and, after washing well and draining on porous porcelain, the substance was finally crystallised from formic acid:

0·1938 gave 0·3285 CO_2 and 0·1115 H_2O. C = 46·2; H = 6·4.
0·2651 „ 0·2114 AgBr. Br = 34·0.
$C_9H_{15}BrO_2$ requires C = 46·0; H = 6·4; Br = 34·0 per cent.

a-Bromo-1-*methyl*cyclo*hexyl*-4-*acetic Acid* melts at 78°, is readily soluble in hot formic acid, and the solution clouds on cooling, but if stirred vigorously the bromo-acid separates in glistening leaflets.

Ethyl a-bromo-1-*methyl*cyclo*hexyl*-4-*acetate* was prepared in two different ways. In the first place the bromo-acid chloride, obtained as described above, was poured into alcohol, and, after remaining for twenty-four hours, the alcoholic solution was diluted with water, the heavy oil extracted with ether, the ethereal extract washed with water and dilute sodium carbonate, dried, and evaporated.

---

* If, however, a crystal is available and is added at this stage, the bromo-acid rapidly crystallises and, after filtering and washing with a little cold formic acid, is almost pure.

The viscid, unpleasant smelling bromo-ester was placed over sulphuric acid in an evacuated desiccator until free from ether.

Subsequently, the bromo-ester was prepared by leaving the solution of the pure bromo-acid in 10 per cent. alcoholic sulphuric acid for three days. The product was diluted with water, the heavy oil extracted with ether, the ethereal solution was washed with sodium carbonate, dried, and evaporated. After remaining for two days over sulphuric acid in an evacuated desiccator, the viscid, almost colourless oil yielded the following result on analysis:

0·2642 gave 0·1851 AgBr. Br = 29·8.

$C_{11}H_{19}O_2Br$ requires Br = 30·4 per cent.

*β-Bromo-1-methyl*cyclo*hexyl-4-acetic Acid.*—This substance was prepared by two different methods, namely, by the action of fuming hydrobromic acid on *β-hydroxymethyl*cyclo*hexylacetic acid* (p. 1077), and on *methyl*cyclo*hexylideneacetic acid* (m. p. 41° of Markwald and Meth, p. 1077).

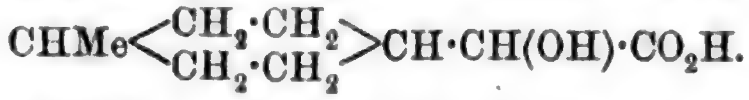
The hydroxy-acid dissolves readily in fuming hydrobromic acid (saturated at 0°), and in a few minutes the solution clouds and crystals begin to form. After adding water, the crystalline precipitate is collected, left in contact with porous porcelain until quite dry, and crystallised, first from formic acid, and then from light petroleum (b. p. 50—60°). From this latter solvent, the substance separates in magnificent, glistening prisms melting at 87°:

0·2120 gave 0·1691 AgBr. Br = 33·9.

$C_9H_{15}O_2Br$ requires Br = 34·0 per cent.

In the second experiment, *methyl*cyclo*hexylideneacetic acid* was finely powdered and stirred with fuming hydrobromic acid (saturated at 0°), when it partly dissolved, and was then converted into an oil, which soon solidified. The product was diluted with water, the precipitate collected, dried on porous porcelain, and then crystallised from light petroleum. The substance separated in glistening prisms, melted at 87°, and was identical with the bromo-acid obtained by the first process. This bromo-derivative has already been prepared by this latter method by Wallach (*Annalen*, 1907, **353**, 312).

*α-Hydroxy-1-methyl*cyclo*hexylacetic Acid,*



$$CHMe<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>CH\cdot CH(OH)\cdot CO_2H.$$

This acid is produced when the corresponding bromo-acid (p. 1081) is boiled with sodium carbonate or dilute potassium hydroxide for about half an hour. The alkaline solution is extracted with ether to remove a trace of neutral oil, acidified, and again extracted four or five times. The ethereal solution is dried and evaporated to a small bulk, when the hydroxy-acid soon separates in colourless, glistening plates. After recrystallisation from ether, the following results were obtained on analysis:

0·1840 gave 0·4202 CO_2 and 0·1508 H_2O. C = 62·3 ; H = 9·1.
0·1825 „ 0·4204 CO_2 „ 0·1510 H_2O. C = 62·8 ; H = 9·2.
$C_9H_{16}O_3$ requires C = 62·8 ; H = 9·3 per cent.

*a-Hydroxy-1-methyl*cyclo*hexyl-4-acetic acid* melts at 148°, and is sparingly soluble in cold water, but dissolves somewhat readily on boiling and separates, when the solution is allowed to cool slowly, in striated plates often aggregated in the form of stars. The solution in dilute sodium carbonate is stable to permanganate.

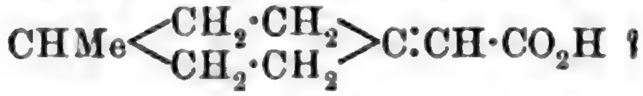
When the powdered acid is stirred with concentrated sulphuric acid, carbon monoxide soon begins to be disengaged, and the evolution is rapid if the mixture is warmed at 40°. If, as soon as the decomposition has ceased, the brown solution is diluted with water, a pleasant smelling oil separates, which is probably the corresponding aldehyde (compare Wallach, *Annalen*, 1906, **347**, 346). At 60—70°, the hydroxy-acid is rapidly decomposed by sulphuric acid, sulphur dioxide is produced, and the solution becomes very dark coloured.

The *silver* salt, $C_9H_{15}O_3Ag$, was obtained as a chalky precipitate when silver nitrate was added to a warm slightly alkaline solution of the ammonium salt. For analysis, the substance was dried first over sulphuric acid and then in the water-oven:

0·3771 gave 0·1460 Ag. Ag = 38·7.
$C_9H_{15}O_3Ag$ requires Ag = 38·7 per cent.

The ethereal mother liquors from the crystallisation of the hydroxy-acid (see above) were evaporated, when a viscid oil remained which soon crystallised. After remaining in contact with porous porcelain for a couple of days, the residue was dissolved in hot water, digested with animal charcoal, and the colourless solution concentrated, when, on cooling, a large quantity of the same hydroxy-acid of melting point 148° separated. It was to be expected that during the bromination of 1-methyl*cyclo*hexyl-4-acetic acid and subsequent conversion of the bromo- into the hydroxy-acid, two stereoisomeric modifications would result, and therefore the mother liquors of the two acids were very carefully investigated, but in neither case could any evidence of the existence of a second modification be obtained.

1-*Methyl*cyclo*hexylidene*-4-*acetic Acid*,



$$\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{C{:}CH\cdot CO_2H}\ ?$$

In our first attempts to prepare this acid, a series of experiments were made with the object of eliminating hydrogen bromide from α-bromo-1-methyl*cyclo*hexyl-4-acetic acid by means of alcoholic potash, diethylaniline, &c., but without success. In the case of diethylaniline, for example, a considerable quantity of a viscid, neutral oil was formed, which had an odour resembling that of oenanthol. When, however, the ester of the bromo-acid was heated with diethylaniline, the reaction appeared to proceed normally.

Ethyl α-bromomethyl*cyclo*hexyl acetate (25 grams) was digested for three hours with freshly-distilled diethylaniline (70 grams), care being taken that both substances were quite dry. The dark brown liquid was dissolved in ether and extracted with hydrochloric acid until quite free from diethylaniline, the ethereal solution was filtered from a little tarry matter, dried, and the ether evaporated. The residual oil was then distilled under reduced pressure, when almost the whole quantity passed over at 156—158° (100 mm.). Two different preparations gave the following analytical results:

0·2085 gave 0·5513 CO_2 and 0·1956 H_2O. C = 72·1; H = 10·4.
0·1664 „ 0·4416 CO_2 „ 0·1542 H_2O. C = 72·3; H = 10·3.
$C_{11}H_{18}O_2$ requires C = 72·5; H = 9·9 per cent.

Ethyl 1-*methyl*cyclo*hexylidene*-4-*acetate* is a colourless oil, which appears to distil under ordinary conditions without decomposition, and possesses in a marked degree the unpleasant odour characteristic of unsaturated esters. The free acid was obtained by digesting the ester (15 grams) with methyl-alcoholic potash (8 grams KOH), when hydrolysis took place rapidly, and, after a few minutes, water was added and the solution evaporated until quite free from methyl alcohol. The alkaline liquid was cooled with ice and acidified with hydrochloric acid, when a crystalline acid separated, which was collected and twice crystallised from formic acid (D = 1·22):

0·1619 gave 0·4142 CO_2 and 0·1380 H_2O. C = 69·8; H = 9·4.
0·1134 „ 0·2903 CO_2 „ 0·0955 H_2O. C = 69·8; H = 9·3.
$C_9H_{14}O_2$ requires C = 70·1; H = 9·1 per cent.

Obtained and purified in this way, *methyl*cyclo*hexylidene*-4-*acetic acid* softens at about 63°, and melts at about 70°; it is readily soluble in warm formic acid, from which it separates as a satiny, crystalline mass, somewhat resembling benzoic acid. It dissolves readily in benzene or light petroleum, but is almost insoluble in cold water. If, however, the acid is boiled with a large volume of a water, the filtered solution deposits a voluminous, crystalline mass, which mats together like cotton wool. The solution of the acid in sodium carbonate decolorises permanganate rapidly, even at 0°.

During the course of this investigation, a considerable quantity (about 20 grams) of the above acid was prepared, but, in spite of repeated recrystallisation from various solvents, the melting point was always unsatisfactory. In order to obtain further evidence of the constitution of this acid, 10 grams were oxidised in dilute alkaline solution by ozone, and, as soon as the ozone passed freely, the solution was diluted, acidified, and placed in the ice-chest. After a few days, a small quantity of a crystalline acid had separated, which, after crystallisation from formic acid, melted at 73°, and was found to consist of 1-methyl*cyclo*hexyl-4-acetic acid:

0·1240 gave 0·3122 CO_2 and 0·1174 H_2O. C = 68·7; H = 10·5.

$C_9H_{16}O_2$ requires C = 69·2; H = 10·2 per cent.

The quantity of this acid obtained was nearly half a gram, and it is therefore obvious that reduction must have taken place to some extent, probably during the elimination of hydrogen bromide from ethyl bromomethyl*cyclo*hexylacetate by diethylaniline. In spite of the analytical data, the methyl*cyclo*hexylideneacetic acid described above is evidently not a pure substance, and the melting point given must therefore be considered as quite unreliable.

The principal product of the oxidation of this acid by ozone is a syrup readily soluble in water, and from which, so far, it has not been found possible to isolate anything crystalline.

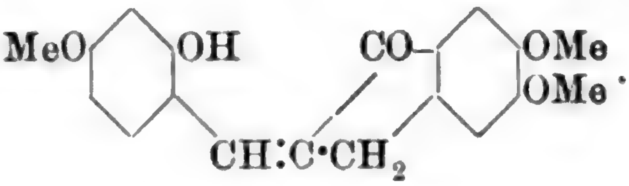
The authors wish to thank Messrs. G. B. Stones and W. N. Haworth for valuable assistance in carrying out the above experiments.

THE UNIVERSITY,
MANCHESTER.

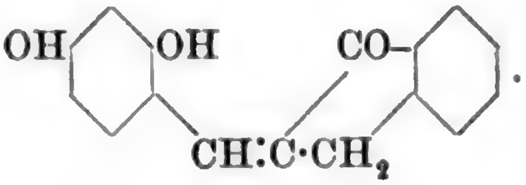
CX.—*The Synthesis and Constitution of Certain Pyranol Salts Related to Brazilein and Haematein.*

By WILLIAM HENRY PERKIN, jun., ROBERT ROBINSON, and (in part) MAURICE RUSSELL TURNER.

DURING the course of synthetical experiments made in connexion with the researches on the constitution of brazilin and hæmatoxylin (Trans., 1908, **93**, 490), we found it necessary to study the condensation of aldehydes with 1-hydrindones, and the results of the first part of this investigation have been published (Trans., 1907, **91**, 1073). Most of these condensations were carried out in the presence of alkali; thus, for example, *p*-methoxysalicylaldehyde and 5 : 6-dimethoxy-1-hydrindone condense in the presence of methyl-alcoholic potash to form 2′-hydroxy-4′ : 5 : 6-trimethoxy-2-benzylidene-1-hydrindone,

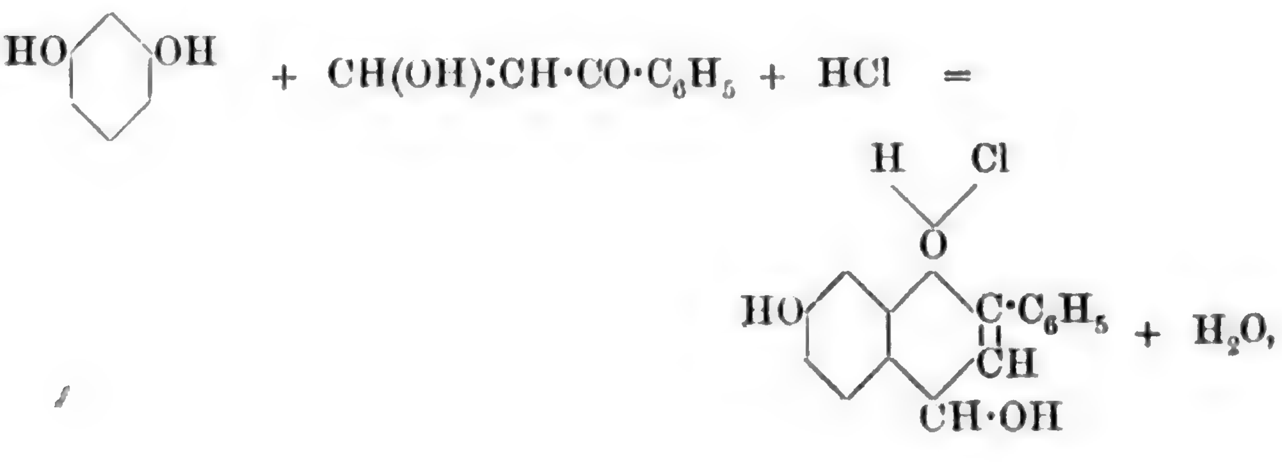


In the case of condensations with *β*-resorcylaldehyde, it was found impossible to employ alkali, and hydrogen chloride was used instead; thus, for example, *β*-resorcylaldehyde and 1-hydrindone condense in the presence of hydrogen chloride in glacial acetic acid to form 2′ : 4′-dihydroxy-2-benzylidene-1-hydrindone hydrochloride (*loc. cit.*, 1092), which, on decomposition with water, yields the unsaturated ketone,

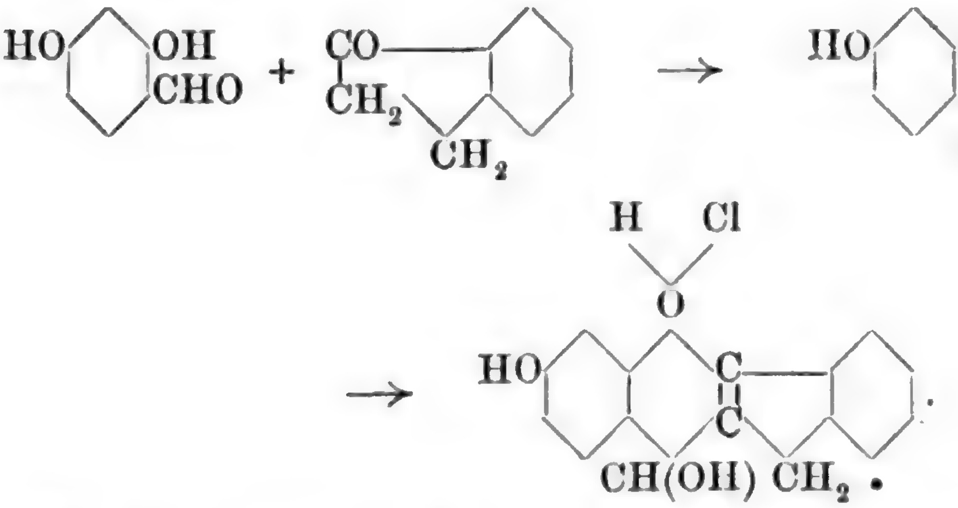


In one experiment, not described in the previous paper, we employed alcoholic hydrogen chloride instead of the glacial acetic acid solution, and found that the result was entirely different, since the product did not deposit crystals, and when diluted with water gave a clear liquid, from which, after some hours, a quantity of orange crystals separated.

In endeavouring to understand this difference in behaviour, we were struck with the similarity in appearance and properties of these orange crystals with the substance which Bülow and Sicherer (*Ber.*, 1901, **34**, 3890) obtained by the interaction of resorcinol and benzoylacetaldehyde in presence of hydrochloric acid. Bülow and Sicherer formulate this process thus:



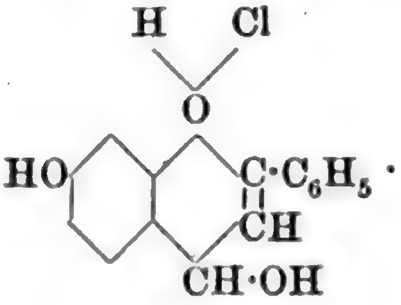
and the product is 7-hydroxy-2-phenylbenzopyranol(1 : 4) hydrochloride. It is an orange, crystalline substance, and its other properties correspond almost exactly with those of our orange crystals. These and other considerations suggested to us that in our experiments also a pyranol derivative had probably been produced, namely, 7-hydroxy-2 : 3-indenobenzopyranol(1 : 4) hydrochloride, a substance which we may, in the meantime, represent as being formed according to the scheme:



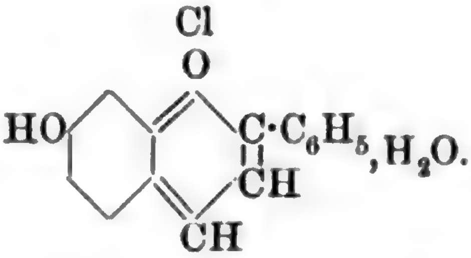
Such a process as this is, of course, unusual, since elimination of water from an aldol grouping generally takes place in such a way that $>CH(OH)\cdot CH<$ becomes $\cdot CH{:}C<$. In order to determine whether such a change as that represented above can actually take place, we investigated the condensation of β-resorcylaldehyde with acetophenone under the same conditions, since, if the process proceeded in the same way in this case also, the product would be the pyranol salt obtained by Bülow and Sicherer, and this we found was the case.

This fact was published in a preliminary communication (Proc., 1907, **23**, 149), and shortly afterwards Decker and von Fellenberg (*Ber.*, 1907, **40**, 3815) investigated this and other analogous cases with the same results. It is clear that this important method of formation of pyranols is a general one. The aldehyde condenses with the ketone to yield an aldol, which, under the influence of hydrogen chloride, undergoes intramolecular change with formation of the pyranol hydrochloride. We have investigated several cases of this kind, and the results are described in detail in the experimental part of this research.

While engaged in this investigation, we became greatly interested in the problem of the mechanism of the formation of these pyranols, and this led us to examine the formation and composition of a variety of salts, many of which are highly interesting. The difficult problem in connexion with these salts is to decide how much water they contain as water of crystallisation. In illustration of this important point, we may take the case of 7-hydroxy-2-phenylbenzopyranol (1 : 4) hydrochloride (p. 1098). The composition of this substance corresponds with the formula

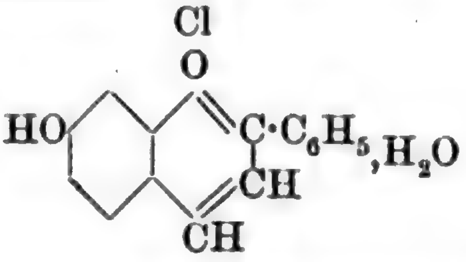


All the hydrochlorides described in this communication could be built up on this type, except that in some cases, as, for example, in the case of 7-hydroxy-2 : 3-indenobenzopyranol (1 : 4) hydrochloride (p. 1100), the salt contains water of crystallisation as well. The question, however, arises whether the above formula really represents the constitution of the hydrochloride, or whether it should be written



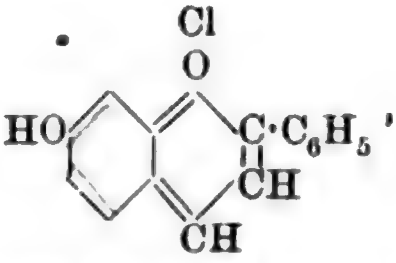
In other words, does the production of the oxonium salt from the pyranol and hydrochloric acid involve the elimination of water, and are these salts, in reality, *anhydrohydrochlorides*?

Decker (*Annalen*, 1907, **356**, 302) considers that this is the case, and he proposed the formula



for the pyranol anhydrohydrochloride, which we have taken as the example.

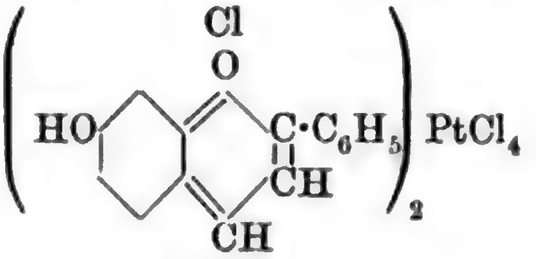
Our view differs from that of Decker, in that we consider that the anhydropyranol salts must be represented as *o*-quinonoid, that is to say, that we represent the anhydrohydrochloride in question as having the constitution



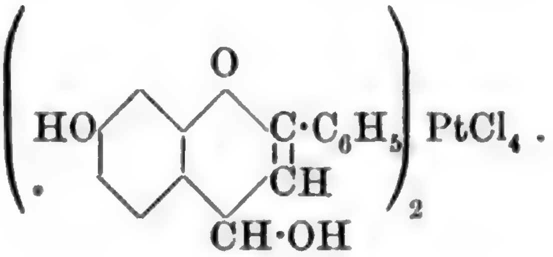
and the reasons for this view are given later (p. 1090).

The evidence at present available is not sufficient to make it possible to decide definitely that the pyranol hydrochlorides are anhydro-salts, but, as there are many considerations which favour this view, we shall, in the following pages, represent them as such.

The colour of the salts is not very much affected, for example, when the anhydrohydrochlorides are converted into double salts, which are unquestionably anhydro-salts, and this certainly denotes similarity in structure. In order to obtain as much evidence as possible bearing on this point, a large number of the double salts of the pyranol anhydrohydrochlorides with platinic chloride, ferric chloride, and, in a few cases also, with gold chloride have been prepared and analysed. The *platinichlorides* are precipitated from solutions of the anhydrohydrochlorides by platinic chloride, and, after drying over sulphuric acid in a vacuum, have the composition $(\text{pyranol,HCl})_2\text{PtCl}_4$. If, however, these salts are recrystallised from dilute hydrochloric acid, they lose water, and have the composition $(\text{pyranol,HCl}-\text{H}_2\text{O})_2\text{PtCl}_4$. The recrystallised platinichloride of 7-hydroxy-2-phenylbenzopyranol (1 : 4) is undoubtedly an anhydro-salt of the formula (I),



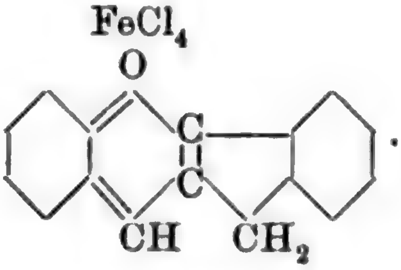
(I.)



(II.)

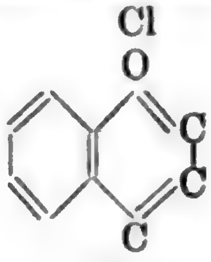
but the salt containing water may either have the constitution (II) or be simply the anhydro-salt plus water of crystallisation.

All the *ferrichlorides* which we have prepared are derivatives of the anhydrohydrochloride; thus, for example, the anhydroferrichloride of 2 : 3-indenobenzopyranol (1 : 4) is represented by the formula

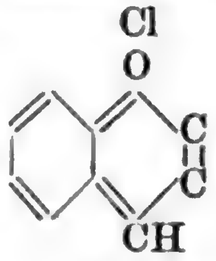


These facts, and other evidence which has gradually accumulated, are clearly strongly in favour of the proposition that the pyranol salts are formed with elimination of water, and are, in fact, anhydro-salts.

If this is the case, the question now arises whether Decker's view of their constitution or our view is correct (p. 1088). There seems to be no reason why substances having the constitution suggested by Decker should be strongly coloured. The linkings in his skeleton formula (III) are in a similar position to those in naphthalene and in quinoline, and these substances do not yield coloured compounds unless, of course, some chromophore be introduced. The system (IV) which we have advocated contains, on the other hand, an *o*-quinonoid structure, and might for this reason be expected to yield strongly coloured derivatives.



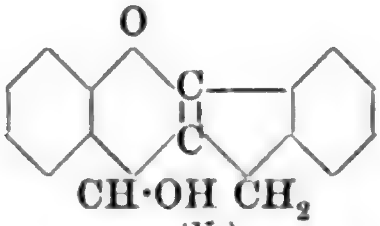
(III.)



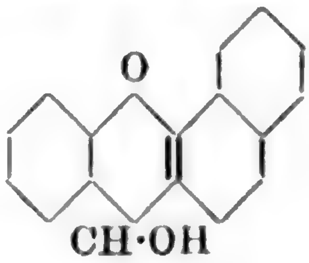
(IV.)

Werner, in a very interesting and important paper (*Ber.*, 1901, **34**, 3303), has shown that xanthhydrol, and especially naphthaxanthhydrol, dissolve in acids with the formation of coloured oxonium salts.

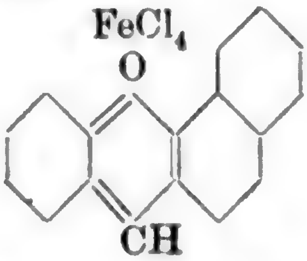
If now the formula of an indenobenzopyranol, for example, 2:3-indenobenzopyranol(1:4) (V) be compared with that of pheno-1:2-naphthaxanthhydrol (VI), it will be seen that the groups essential to our argument are the same in both cases. The anhydroferrichloride of naphthaxanthhydrol is exactly similar to that of indenobenzopyranol, since both crystallise well from acetic acid, are highly coloured, and have the composition of anhydro-salts. But the anhydroferrichloride of naphthaxanthhydrol can only be *o*-quinonoid, whether it be represented by the formula



(V.)

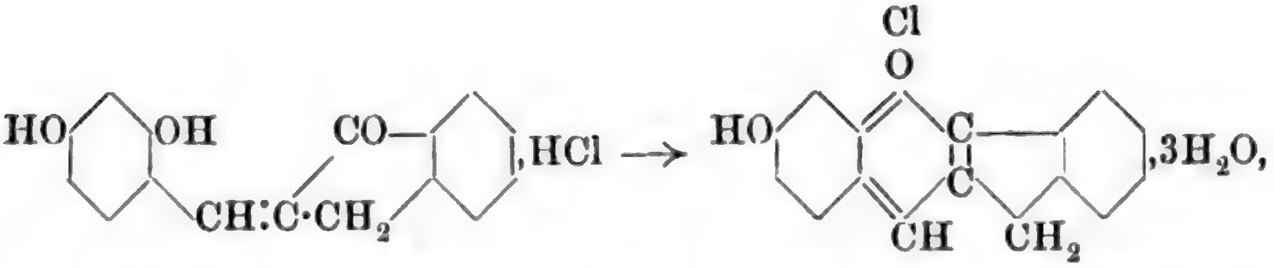


(VI.)

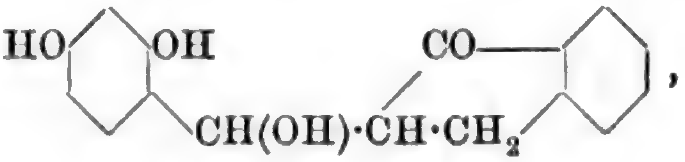


or with the double linkings arranged in connexion with the naphthalene nucleus. Since, then, such an arrangement is associated with highly coloured salts, we consider that this, although indirect, is strong evidence in favour of our view that the anhydropyranol salts have an *o*-quinonoid structure.

The next important step in connexion with the problem of the mechanism of the formation of anhydropyranol salts was the observation which we have made that the unsaturated ketones can be readily converted into anhydropyranol salts by the action of hydrochloric acid. When, for example, 2′ : 4′-dihydroxy-2-benzylidene-1-hydrindone (Trans., 1907, **91**, 1093) is boiled with hydrochloric acid, it is converted into 7-hydroxy-2 : 3-indenobenzopyranol (1 : 4) anhydrohydrochloride :



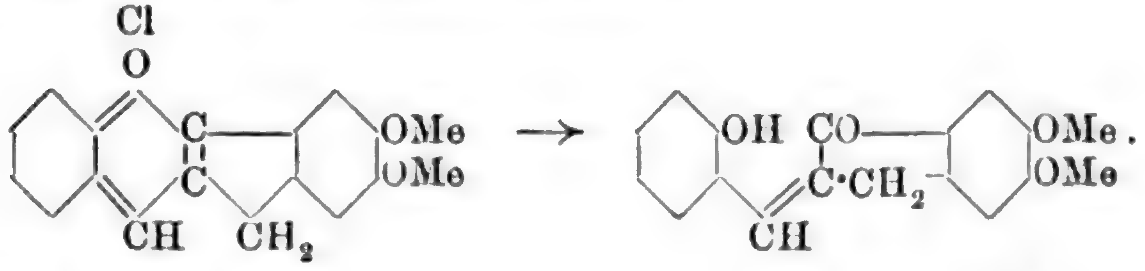
that is to say, into the substance which is obtained by the condensation of β-resorcylaldehyde and 1-hydrindone in presence of hydrochloric acid. It might be urged that the intermediate aldol condensation product :



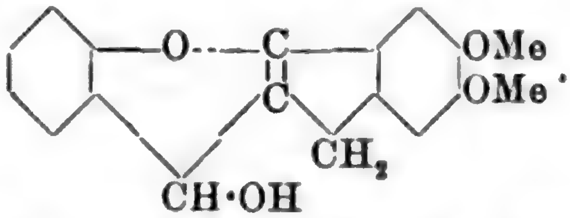
doubtless formed in this latter condensation, is next converted into the unsaturated ketone hydrochloride, and that this then yields the anhydropyranol salt owing to the continued action of the hydrochloric acid, in which case the two methods of formation would be identical. This view does not, however, appear to be the correct one, because the unsaturated ketone hydrochloride is a deep red substance and changes into the anhydropyranol salt only gradually, whereas the condensation between β-resorcylaldehyde and 1-hydrindone is very rapid, and there is no appearance of an intermediate red substance being formed. These observations could always be made during the many condensations of a similar character which we have investigated, and the difference between the slow rate of the formation of the pyranol anhydrohydrochloride from the unsaturated ketone and its rapid formation by the condensation of the aldehyde and ketone is especially marked in the case of the synthesis of 4′ : 5′ : 7-trimethoxy-2 : 3-indenobenzopyranol (1 : 4) anhydrohydrochloride (p. 1106).

We next found that the unsaturated ketones can be regenerated from the pyranol salts by the action of alkali.

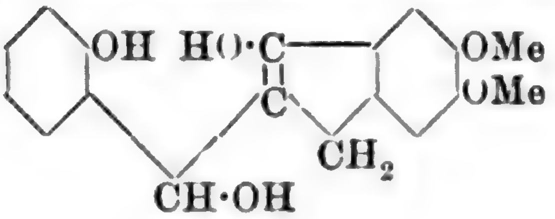
Thus 4′ : 5′-dimethoxy-2 : 3-indenobenzopyranol (1 : 4) anhydrohydrochloride (p. 1103), on treatment with alcoholic potash, yields 2′-hydroxy-5 : 6-dimethoxy-2-benzylidene-1-hydrindone :



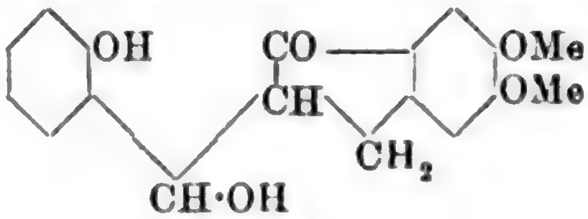
This change requires some explanation. The first product is the pseudo-base, or, in other words, the pyranol *:



This substance is then hydrolysed and converted into I, which,



(I.)



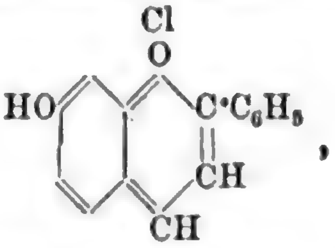
(II.)

in its tautomeric form, II, loses water in the presence of alkali, with formation of the potassium salt of the unsaturated ketone.

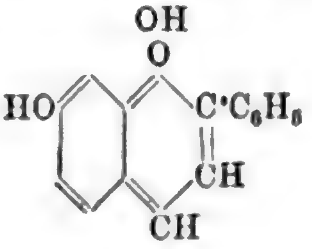
During the course of our experiments, we have obtained further evidence of considerable interest bearing, not only on several of the questions already discussed, but, more particularly, on the mechanism of the formation of anhydropyranol hydrochlorides from unsaturated ketones. Our experiments show that when a pyranol is made from

---

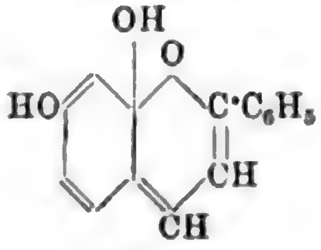
* In the scheme given above, we have represented the pyranol pseudo-base in the usual manner, but there are reasons for doubting whether this formula is the correct one. It does not, for example, account for the intense colour characteristic especially of the *hydroxypyranol* bases. The first product of the action of alkali on such a salt as 7-hydroxy-2-phenylbenzopyranol (1 : 4) anhydrohydrochloride,



is probably the oxonium hydroxide (I), which might well be converted by isomeric change into the expression (II), and this, not improbably, represents the true constitution of the pyranol pseudo-base.



(I.)



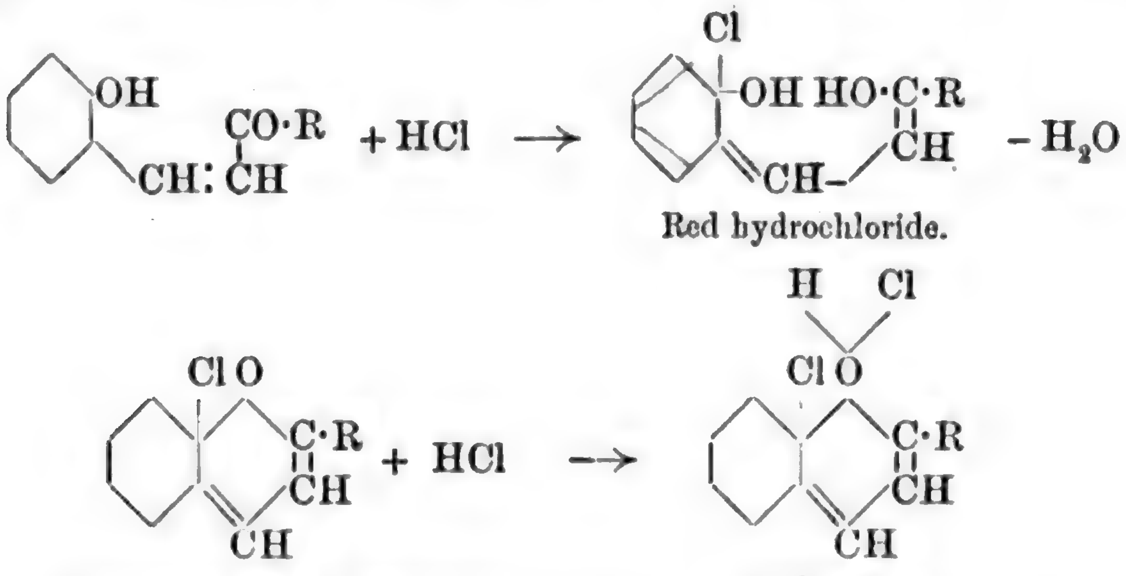
(II.)

This formula contains an *o*-quinonoid grouping and accounts well for the coloured nature and other properties of the pyranols. This scheme also seems to be of wide application, not only to the pyranols, but also to other coloured pseudo-bases. The colour of all substances of this class is influenced and intensified in a marked degree by the presence of (auxochromic) hydroxy-groups in the *o*-quinonoid nucleus, whereas hydroxy-groups in the other nucleus exercise little influence on the colour.

an unsaturated ketone by the action of hydrochloric acid, the first step is the production of a ketone hydrochloride, which by the further action of hydrochloric acid is converted into a dichloride.

2-Hydroxybenzylidene-2′ : 4′-dimethoxyacetophenone, for example, yields a red, crystalline hydrochloride when its solution in glacial acetic acid is saturated with hydrogen chloride, and this hydrochloride is readily decomposed by water into the ketone and hydrochloric acid. When this red salt is warmed in acetic acid solution at 50°, the colour becomes orange-red, a change which is due, as will be directly explained, to the formation of an oxonium salt.

If, in the above experiment, ordinary concentrated hydrochloric acid is employed, the same red substance is obtained, and, on warming, this dissolves with formation of an orange solution, from which a red, crystalline substance separates on cooling. This substance has the composition $C_{17}H_{16}O_3Cl_2,2H_2O$, and, when treated with water, the extra chlorine atom is removed with the formation of the anhydropyranol hydrochloride. Other unsaturated ketones exhibit an exactly similar behaviour under the above conditions, and we are of opinion that these interesting changes are to be explained in the following way:

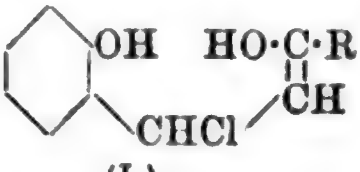


Red hydrochloride.

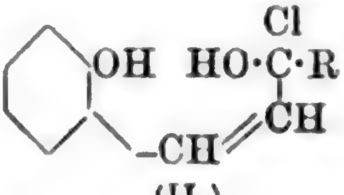
Oxonium base of dichloride.

Dichloride.

In examining this series of changes, it will be convenient, in the first place, to discuss the constitution of the ketone hydrochlorides, and, in attempting this difficult problem, one fact must especially be kept in view, namely, that the hydrochloride must be so formulated as to be capable of losing water with the formation of a closed oxygen ring. There are six formulæ which appear to satisfy this condition:

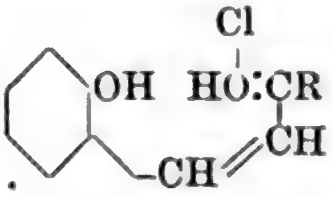


(I.)

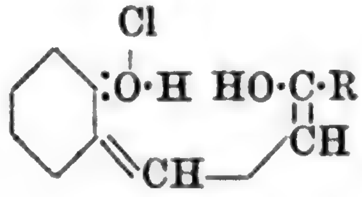


(II.)

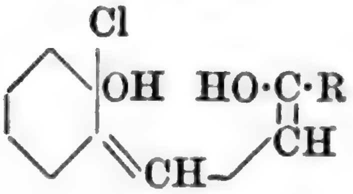
by Google



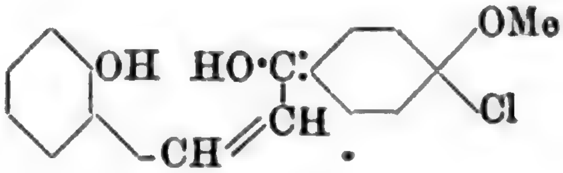
(III.)



(IV.)



(V.)



(VI.)

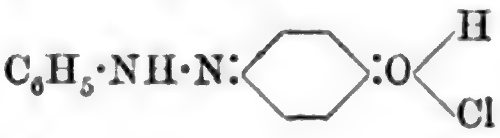
Against I, II, and III it may be urged that the chromophoric grouping contained in either of these is not sufficient to account for the striking red colour of the salts of the unsaturated ketone.

Probably III would be the most highly coloured, but hardly more so than the unsaturated ketone from which it is derived.

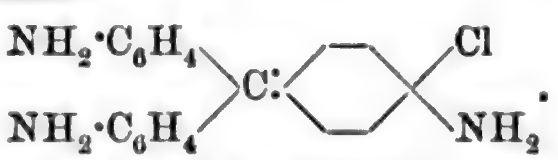
Formula VI can hardly be correct, because it is well known that the second aromatic nucleus is not essential to the formation of coloured salts. Thus dibenzylideneacetone forms coloured salts with mineral acids, and the same is true of anisylideneacetone.

Formulæ IV and V both exhibit an *o*-quinonoid structure, and may therefore well explain the deep colour of the salts of unsaturated ketones. It is difficult to decide between these two formulæ, and, before attempting to do so, we propose to consider whether the arguments which have so frequently been urged against the *o*-quinonoid structure for coloured substances are to be accepted.

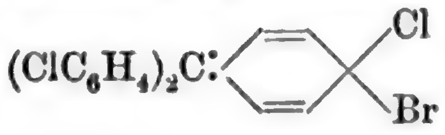
There are several classes of substances the salts of which have been recognised as probably being carbonium or oxonium compounds. Thus Fox and Hewitt (Trans., 1908, **93**, 337) assign formulæ such as

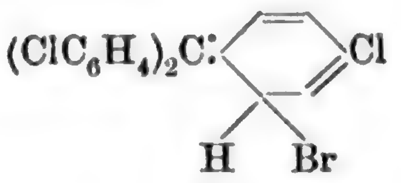


to the hydrochlorides of hydroxyazo-compounds. Rosaniline salts are considered by Baker (Trans., 1907, **91**, 1499) to be carbonium salts derived from the scheme



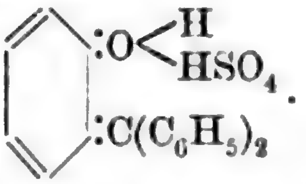
But it is especially the non-nitrogenous derivatives of triphenylcarbinol which have been most completely investigated from this point of view, and the evidence which has accumulated certainly seems to prove that the triphenylcarbinol salts are not *p*-quinonoid in structure. Baeyer (*Ber.*, 1907, **40**, 3083) and also Tschitschibabin (*Ber.*, 1907, **40**, 3965) have investigated tri-*p*-chlorophenylcarbinol, and they find that its hydrobromide and sulphate do not lose chlorine when treated with silver nitrate or other similar reagents. This behaviour clearly proves that the hydrobromide of tri-*p*-chlorophenylcarbinol cannot be represented by the *p*-quinonoid formula (I).


(I.)


(II.)

This and all other similar arguments which have, so far, been brought forward do not, however, in our opinion hold against the *o*-quinonoid structure (II).

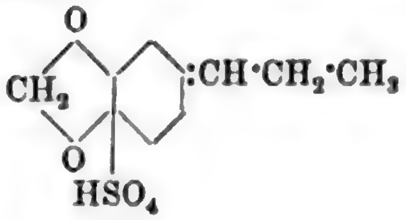
Baeyer and Villiger (*Zeitsch. angew. Chem.*, 1906, **19**, 1287) have suggested an *o*-quinonoid structure for the salts of *o*-hydroxytriphenylcarbinol, but afterwards rejected it. This substance dissolves in acetosulphuric acid with the formation of an intensely red salt, but no indication of the intermediate formation of a quinone could be observed when the salt was decomposed by water. Baeyer and Villiger conclude that this behaviour is a clear proof that the red salt cannot have the constitution:

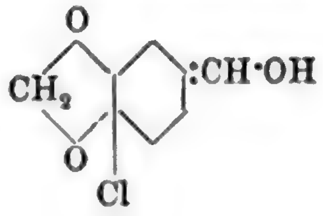


It seems to us, however, that it is very doubtful whether a salt of this formula would give a yellow quinone when decomposed by water, and even if it did, the yellow quinone might be very unstable and immediately pass into the colourless carbinol, and thus escape detection. As far, therefore, as we are able to judge, there are no sound reasons against ascribing an *o*-quinonoid structure to the salts of triphenylcarbinol or dibenzylideneacetone, and, indeed, there seems every reason to believe that both *o*- and *p*-quinonoid structure must be accepted in explanation of colour or the formation of coloured salts.* As the result of these and other considerations, we are strongly inclined to the opinion that *o*-quinonoid structure is probably the reason for the colour of the salts of unsaturated

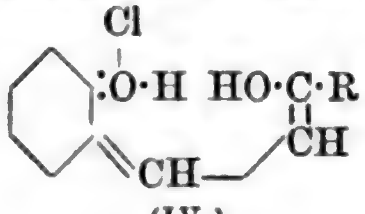
---

* In the case of the salts of some unsaturated compounds, the structure may well be *p*-quinonoid. Thus the sulphate of *iso*safrole may, not improbably, have the formula (I), and the coloured hydrochloride of the corresponding aldehyde may have the constitution (II):

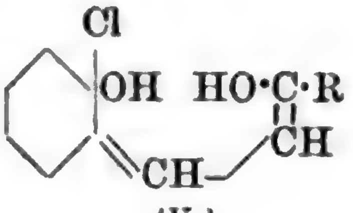

(I.)


(II.)

ketones, and we therefore selected formulæ IV and V as the only possible expressions for the hydrochlorides.

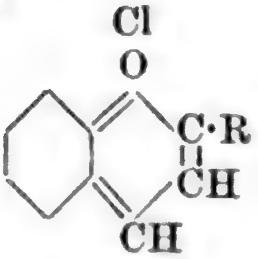


(IV.)



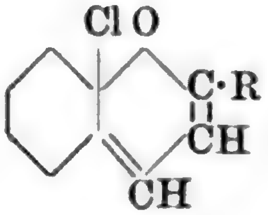
(V.)

When water is eliminated from these expressions, we arrive at the formulæ



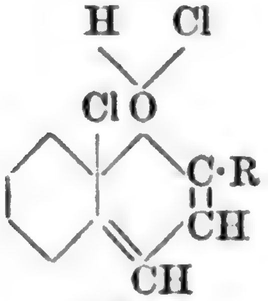
(VII.)

and

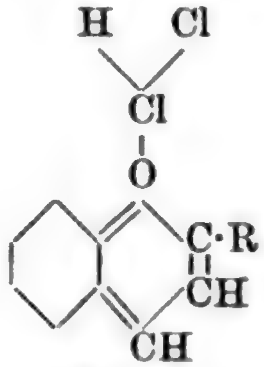


(VIII.)

for the base of the dichloride, and from these the structure of the dichloride itself is obtained by the addition of hydrogen chloride. In the case of VIII, this formation of the oxonium salt is simply due to the addition of hydrogen chloride to the oxygen atom in the usual manner:



(IX.)

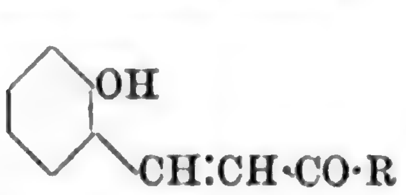


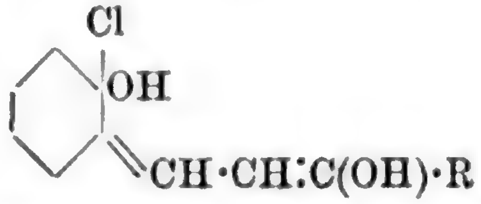
(X.)

but in the case of VII the hydrochloride must be formed by the addition of hydrogen chloride to the chlorine atom, which thus becomes tervalent. It is not possible to decide definitely, at present, between these two formulæ, and it would, indeed, be difficult to suggest a line of experimental inquiry which could distinguish between two such expressions. Several considerations which have been indicated in the foregoing pages seem to us to point rather to IX as the correct expression, and we have therefore adopted formulæ based on this in the present paper.

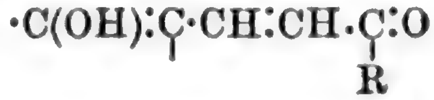
Many interesting considerations arise from the study of the mechanism of the formation of the pyranol anhydro-salts, and there is one point to which we should like to direct special attention in the present communication. The selection of IX as the formula for the dichloride does not definitely decide whether IV or V (p. 1096) represents the unsaturated ketone hydrochloride, but it is obvious that

IV is the more probable. If this formula be compared with that of the unsaturated ketone:



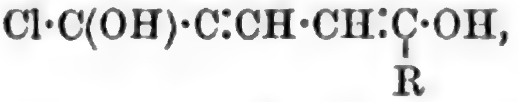


the addition of hydrogen and chlorine in the formation of the hydrochloride appears, at first sight, to be unusual. This difficulty, however, at once disappears when the change is compared with that which is so well known to take place in systems containing conjugated double linkings. In the case under discussion, the system



$$\cdot C(OH){:}\underset{|}{C}\cdot CH{:}CH\cdot\underset{\underset{R}{|}}{C}{:}O$$

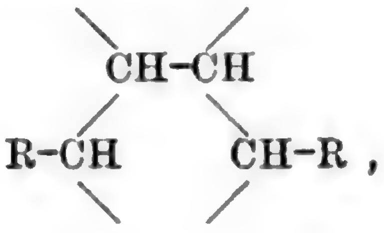
becomes



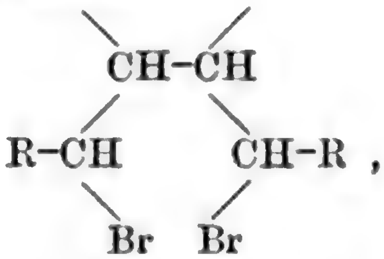
$$Cl\cdot C(OH)\cdot C{:}CH\cdot CH{:}\underset{\underset{R}{|}}{C}\cdot OH,$$

that is to say, the addition of hydrogen chloride takes place at the extreme ends of a system of three double linkings. In considering this case and the analogous case of substances which contain two conjugated double linkings, it has occurred to us that the theory of partial valency worked out by Thiele is unnecessarily complicated, and this led us to devise the following simple explanation, which is based on the usual spacial conceptions.

If in the case $R\cdot CH{:}CH\cdot CH{:}CH\cdot R$ we write free valencies in the place of the double linkings and adopt the "Spannungs Theorie" of Baeyer, we obtain the scheme

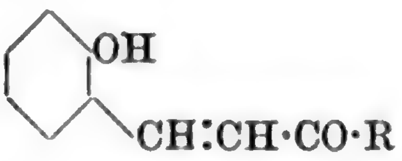


and it is now only necessary to assume that the addition of two atoms of bromine, for example, takes place to the free valencies which are closest together or can be brought together with the least strain, and we obtain as the additive product

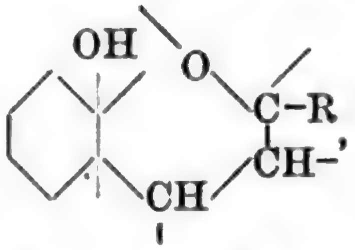


and if we employ the ordinary method of expression this becomes $R\cdot CHBr\cdot CH{:}CH\cdot CHBr\cdot R.$

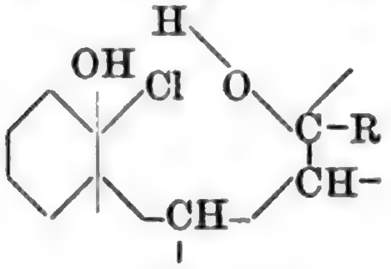
When this method of representation is applied to the case of the unsaturated ketone, its formula



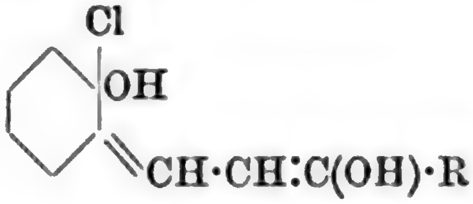
becomes



and the addition of hydrogen chloride again takes place to those free valencies which approximate most closely to one another, and leads to the formula (I) for the hydrochloride, which, expressed in the ordinary way, becomes (II). We have satisfied ourselves that other changes, due to the addition of halogens, halogen acids, &c., to systems of conjugated double linkings, may be equally well explained in this simple manner.



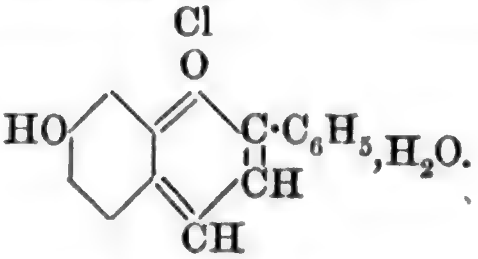
(I.)



(II.)

Experimental.

7-*Hydroxy-2-phenylbenzopyranol* (1 : 4) *Anhydrohydrochloride*,



This substance is readily obtained when acetophenone (5 grams) and β-resorcylaldehyde (5 grams) are dissolved in glacial acetic acid (25 c.c.) and a slow stream of hydrogen chloride is passed into the cooled solution. The liquid becomes yellow and then red, and, in a few hours, orange-yellow crystals separate. After standing overnight, these are collected, washed with acetic acid, and recrystallised from very dilute hydrochloric acid.

This hydrochloride is identical with that obtained by Bülow and Sicherer (*Ber.*, 1901, **34**, 3889) by the condensation of resorcinol with benzoylacetaldehyde in the presence of hydrochloric acid, a fact which was proved by direct comparison of samples of this substance obtained by the two processes * and by the following analysis:

---

* Bülow and Sicherer state that this hydrochloride melts at 152—153°, but all the specimens we prepared darkened at about this temperature without exhibiting a definite melting point.

0·1717 gave 0·0896 AgCl. Cl = 12·7.

$C_{15}H_{12}O_3$,HCl requires Cl = 12·7 per cent.

The orange-red *platinichloride* was also prepared and analysed:

0·1889 gave 0·0412 Pt. Pt = 21·8.

$(C_{15}H_{11}O_2Cl)_2PtCl_4,2H_2O$ requires Pt = 21·7 per cent.

When this salt is crystallised from formic acid, in which it is sparingly soluble, it is obtained in deep orange crystals, which, after drying at 100°, gave on analysis:

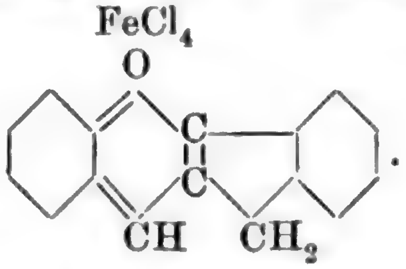
0·2150 gave 0·0492 Pt. Pt = 22·9.

$(C_{15}H_{11}O_2Cl)_2PtCl_4$ requires Pt = 22·8 per cent.

This interesting result shows that this platinichloride exists in two modifications, and, after crystallisation, is the anhydro-compound.

It is doubtful whether the substance which Bülow and Sicherer (*loc. cit.*, p. 3895) obtained by methylating the above pyranol is a true 7-methyl ether, because their product did not fluoresce in concentrated sulphuric acid solution. 7-Methoxy-2-phenylbenzopyranol(1 : 4), prepared from acetophenone and *p*-methoxysalicylaldehyde, shows in sulphuric acid solution a very intense, bluish-green fluorescence, which is not destroyed by dilution with water.

2 : 3-*Indenobenzopyranol* (1 : 4) *Anhydroferrichloride*,



In order to prepare this substance, 2 grams of 2′-hydroxybenzylidene-α-hydrindone (Trans., 1907, **91**, 1087) are dissolved in alcohol (50 c.c.), and concentrated hydrochloric acid (25 c.c.) is then added to the boiling solution. The liquid is then boiled for ten minutes and diluted with an equal volume of water. The substance is now present as an oxonium salt (compare p. 1090), and therefore no separation occurs.

On the addition of ferric chloride, a voluminous, yellow precipitate is obtained, which is collected and crystallised from glacial acetic acid. It is moderately soluble in the hot solvent, but very sparingly so in the cold. After drying at 100°, the bright yellow, glistening plates gave, on analysis, the following results:

0·1221 gave 0·2063 CO_2 and 0·0297 H_2O. C = 46·1; H = 2·7.

$C_{16}H_{11}O,FeCl_4$ requires C = 46·0; H = 2·6 per cent.

This *anhydroferric* salt is somewhat soluble in water, but very sparingly so in water containing hydrochloric acid. It melts, apparently without decomposition, at 175°. When this salt or a drop of the oxonium solution is dissolved in sulphuric acid, the solution shows a splendid blue fluorescence.

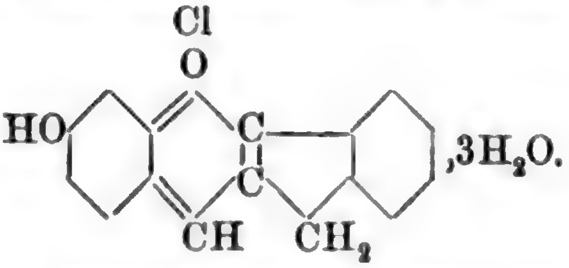
The *platinichloride.*—When platinic chloride is added to the oxonium solution, obtained as described above, orange-yellow crystals gradually separate, and may be recrystallised from hot formic acid, in which the platinichloride is only moderately soluble.

The orange prisms, after drying at 100°, gave on analysis:

0·1281 gave 0·2129 CO_2 and 0·0310 H_2O. C = 45·3; H = 2·7.

$(C_{16}H_{11}OCl)_2PtCl_4$ requires C = 45·4; H = 2·5 per cent.

7-*Hydroxy*-2 : 3-*indenobenzopyranol* (1 : 4) *Anhydrohydrochloride,*



This substance is obtained by the condensation of β-resorcylaldehyde with α-hydrindone in the presence of hydrogen chloride.

α-Hydrindone (2 grams) and β-resorcylaldehyde (2 grams) are dissolved in methyl alcohol (30 c.c.), and hydrogen chloride is passed sufficiently rapidly to raise the solution to the boiling point. The liquid becomes dark reddish-orange, and acquires a green fluorescence. After half an hour, the product is poured into hot dilute hydrochloric acid (200 c.c.), rapidly filtered, and the filtrate allowed to cool slowly, when brownish-orange groups of crystals separate. The crystals (3·5 grams) are collected and recrystallised from hot dilute methyl alcohol containing hydrochloric acid, when brownish-orange, glistening prisms are obtained. After being dried over sulphuric acid in a vacuum desiccator:

0·1190 gave 0·2590 CO_2 and 0·0564 H_2O. C = 59·5; H = 5·2.

0·2142 „ 0·0945 AgCl. Cl = 10·8.

$C_{16}H_{11}O_2Cl.3H_2O$ requires C = 59·3; H = 5·2; Cl = 10·8 per cent.

The constitution of this pyranol hydrochloride is proved by the fact that it is formed when a stream of hydrogen chloride is passed through a solution of 2′ : 4′-dihydroxy-2-benzylidene-1-hydrindone (Trans., 1907, **91**, 1092) in methyl alcohol (50 c.c.) for one hour. After dilution with an equal volume of hot water, the liquid was filtered rapidly and allowed to cool slowly, when the pyranol hydrochloride separated in brownish-orange crystals, and was identical in all respects with the specimen prepared by the process first described above:

0·2340 gave 0·1010 AgCl. Cl = 10·6.

These analyses prove that this pyranol hydrochloride crystallises with three molecules of water. In its properties it is very similar to the hydrochloride of 7-hydroxy-2-phenylbenzopyranol (1 : 4), and shares with that substance and with all the pyranol hydrochlorides described in this paper, the property, in a finely-divided state, of causing violent sneezing. It dissolves in sulphuric acid with a very beautiful bluish-green fluorescence, which is bluer than that exhibited by its methoxy-derivative (p. 1102). The solution of the hydrochloride in a little water is yellow, but dilution causes the colour to become red, showing that dissociation into the base and hydrochloric acid has commenced. The addition of acid reproduces the yellow colour, and the salt crystallises out; on the other hand, much water completely dissociates the salt, and the red base is precipitated.

The hydrochloride darkens at 105°, and, on further heating, gradually shrinks without showing a definite melting point.

The *platinichloride* is obtained when a hot solution of the hydrochloride in dilute hydrochloric acid is mixed with platinic chloride as a yellow, crystalline precipitate, which was collected and well washed. It is sparingly soluble, but may be recrystallised from hot water containing hydrochloric acid and platinic chloride.

For analysis, the precipitate was dried over sulphuric acid in a vacuum desiccator:

0·1626 gave 0·0346 Pt. Pt = 21·3.

$(C_{16}H_{11}O_2Cl)_2PtCl_4,2H_2O$ requires Pt = 21·3 per cent.

The *aurichloride*.—This double salt was prepared by adding a solution of gold chloride to a hot solution of the pyranol hydrochloride in dilute hydrochloric acid. A bright yellow, crystalline precipitate separated at once, and was collected, washed, and dried in a vacuum over sulphuric acid:

0·2079 gave 0·0670 Au. Au = 32·2.

$C_{16}H_{11}O_2Cl,AuCl_3,2H_2O$ requires Au = 32·4 per cent.

This aurichloride appears therefore to contain water of crystallisation.

When this salt is crystallised from methyl alcohol and dilute hydrochloric acid, it undergoes a remarkable change, and is obtained in orange crystals, which, after drying over sulphuric acid, gave the following results on analysis:

0·1135 gave 0·1911 CO_2 and 0·0329 H_2O. C = 45·9; H = 3·2.

0·1908 „ 0·0434 Au. Au = 22·7.

$(C_{16}H_{11}O_2Cl)_2AuCl_3$ requires C = 45·5; H = 2·6; Au = 23 4 per cent.

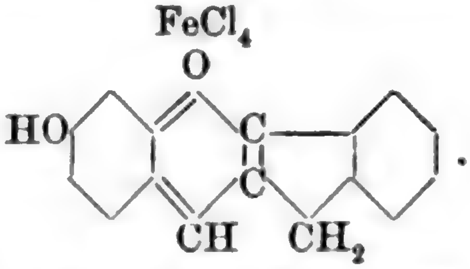
These numbers, although not quite sharp, clearly indicate that the salt, after crystallisation, has the above complex and unusual composition.

The *anhydroferrichloride* is obtained as a brownish-yellow precipitate by adding a concentrated solution of ferric chloride to a strongly acid solution of the hydrochloride. The double salt is collected and crystallised from acetic acid, from which it separates in light brown needles. It darkens at 165°, melts at 171°, and decomposes a few degrees above this temperature. Dried at 100°, it yielded the following results on analysis :

0·1197 gave 0·1967 CO_2 and 0·0292 H_2O. C = 44·8 ; H = 2·7.

$C_{16}H_{11}O_2,FeCl_4$ requires C = 44·5 ; H = 2·6 per cent.

Whilst therefore the platini- and auri-chlorides are derived from the pyranol itself, the ferrichloride is a derivative of the anhydrobase, and its constitution is probably represented by the formula



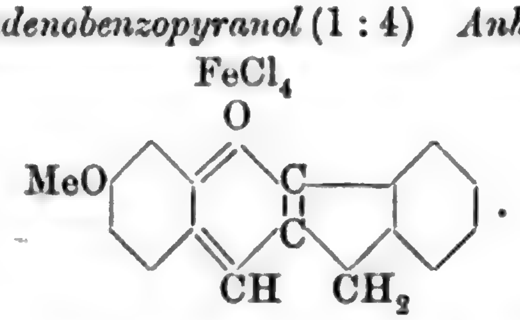
The *pyranol base*, 7-hydroxy-2 : 3-indenobenzopyranol(1 : 4), was prepared by adding sodium acetate to the solution of the hydrochloride. The red precipitate was collected and found to be amorphous. It was, however, pure, since a specimen dried over sulphuric acid in a vacuum gave, on analysis, the following results :

0·1335 gave 0·3719 CO_2 and 0·0583 H_2O. C = 76·0 ; H = 4·8.

$C_{16}H_{12}O_3$ requires C = 76·2 ; H = 4·7 per cent.

Hydrolysis by Potassium Hydroxide.—When the pyranol hydrochloride (1 gram) is boiled with 20 per cent. potassium hydroxide (25 c.c.) for fifteen minutes in a reflux apparatus and distilled in steam, the distillate contains α-hydrindone. This was recognised by the odour and by conversion into the phenylhydrazone, which melted at 130°.

7-Methoxy-2 : 3-indenobenzopyranol (1 : 4) *Anhydroferrichloride*,



This methyl derivative of the anhydroferric salt described above is obtained when 2′-hydroxy-4′-methoxy-2-benzylidene-1-hydrindone (Trans., 1907, **91**, 1091), dissolved in the least possible quantity of boiling alcohol, is gradually mixed with half the volume of concentrated hydrochloric acid. The reaction is complete as soon as the yellow solution gives no precipitate on dilution with water.

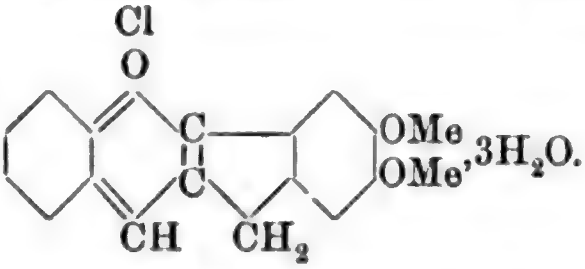
Ferric chloride solution is now added in great excess, the yellow, crystalline precipitate collected, and crystallised from acetic acid. For analysis, the salt was dried at 100°:

0·1214 gave 0·2030 CO_2 and 0·0321 H_2O. C = 45·6; H = 2·9.

$C_{17}H_{13}O_2,FeCl_4$ requires C = 45·8; H = 2·9 per cent.

This *anhydroferrichloride* crystallises in beautiful minute, golden-orange prisms, and is moderately soluble in hot acetic acid or water. It melts without decomposition at 163°, and its solutions, even the dilute aqueous solution, exhibit a remarkably intense bluish-green fluorescence.

4′ : 5′-*Dimethoxy*-2 : 3-*indenobenzopyranol* (1 : 4) *Anhydrohydrochloride*,



Salicylaldehyde condenses very readily with 5 : 6-dimethoxy-1-hydrindone, under the following conditions, with formation of the above hydrochloride. Equal weights of the two substances are dissolved in ten times their weight of ethyl alcohol, and a rapid stream of hydrogen chloride is passed through the solution. The hot liquid becomes dark orange, and in a short time a mass of crystals separates. When cold, the beautiful glistening, orange mass is collected and is nearly pure, but, for analysis, it was recrystallised from dilute alcoholic hydrochloric acid and dried over sulphuric acid in a vacuum:

0·1621 gave 0·3488 CO_2 and 0·0860 H_2O. C = 58·7; H = 5·9.

0·1752 „ 0·0709 AgCl. Cl = 9·9.

$C_{18}H_{15}O_3Cl,3H_2O$ requires C = 58·7; H = 5·7; Cl = 9·7 per cent.

This hydrochloride usually crystallises in orange plates or needles, but when rapidly crystallised from water it separates in microscopic threads. It begins to darken at 135°, and decomposes vigorously at 165°, exhibiting a pure green fluorescence when a trace is dissolved in sulphuric acid. It dissolves in water without fluorescence, and the addition of hydrochloric acid causes the salt to separate. The aqueous solution gives red precipitates with potassium iodide, sulphate, chromate, ferricyanide, nitrate, and other salts. The iodide is especially sparingly soluble, and therefore separates from very dilute solutions. Mercuric chloride gives with an aqueous solution of the hydrochloride a yellow precipitate of the double salt, and addition of sodium acetate or dilute alkali to the solution of the hydrochloride causes a yellowish-brown, amorphous precipitate of the pyranol base to separate.

The *platinichloride* is prepared by adding platinic chloride to the solution of the hydrochloride in hot dilute hydrochloric acid.

An immediate yellow precipitate is obtained, and is collected, washed with dilute hydrochloric acid, and dried in a vacuum over sulphuric acid:

0·3048 gave 0·0624 Pt. Pt = 19·4.

$(C_{18}H_{15}O_3Cl)_2PtCl_4,2H_2O$ requires Pt = 19·4 per cent.

The *anhydroferrichloride* is obtained as an orange precipitate when ferric chloride is added to a strongly acid solution of the hydrochloride. It separates from a large quantity of acetic acid in reddish-brown needles, and, after drying at 100°, gave the following results on analysis:

0·1155 gave 0·1915 CO_2 and 0·0340 H_2O. C = 45·2; H = 3·2.

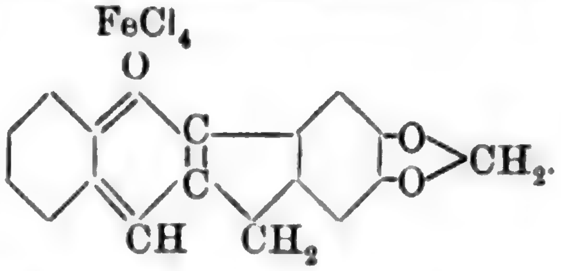
$C_{18}H_{15}O_3,FeCl_4$ requires C = 45·5; H = 3·1 per cent.

This salt is sparingly soluble in hot acetic acid or water and almost insoluble in most other solvents. It begins to darken at about 215°, and has no definite melting point.

Decomposition of the Pyranol by Hydrolysis.—When the pyranol hydrochloride is boiled for half an hour with alcoholic potash (5—10 per cent.), an orange solution is obtained, which gives no precipitate on the addition of water. The solution contains the potassium salt of 2′-hydroxy-5 : 6-dimethoxy-2-benzylidene-1-hydrindone, and this substance separates as a yellow precipitate on the addition of acetic acid. The precipitate was collected and boiled with acetic anhydride and sodium acetate for ten minutes. The product was poured into water and the acetate crystallised from alcohol, when it melted at 180°, and the melting point was unaltered by admixture with the specimen of this acetate previously prepared (Trans., 1907, **91**, 1096). The reverse change, namely, the conversion of 2′-hydroxy-5 : 6-dimethoxy-2-benzylidene-1-hydrindone into 4′ : 5′-dimethoxy-2 : 3-indenobenzopyranol (1 : 4) hydrochloride, was carried out as follows.

Hydroxydimethoxybenzylidenehydrindone (5 grams) was suspended in methyl alcohol (300 c.c.), and a current of hydrogen chloride passed sufficiently rapidly to cause the methyl alcohol to boil. The brick-red precipitate of the ketone hydrochloride (Trans., 1907, **91**, 1095), which soon separated, gradually passed into solution, and the passage of the gas was continued until a sample of the liquid remained clear on dilution with water. The dark yellowish-brown solution was then diluted with water, when, on standing, the pyranol salt crystallised out in the characteristic orange crystals. Careful comparison showed that this salt was identical with the hydrochloride prepared as described on p. 1103.

4′ : 5′-*Methylenedioxy*-2 : 3-*indenobenzopyranol* (1 : 4) *Anhydroferrichloride*,



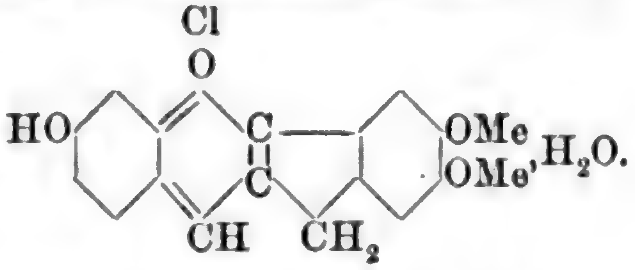
This substance is obtained when 2′-hydroxy-5 : 6-methylenedioxy-2-benzylidene-1-hydrindone (1 gram: compare Trans., 1907, **91**, 1097) is suspended in alcohol (200 c.c.) and concentrated hydrochloric acid (50 c.c.) added. The liquid is boiled for about an hour and until the brick-red hydrochloride, which separates at first, has passed into solution. Concentrated ferric chloride is then added to the yellow solution, and the orange precipitate collected and crystallised from much glacial acetic acid. The deep red, minute prisms were dried at 100°:

0·1168 gave 0·1913 CO_2 and 0·0254 H_2O. C = 44·7 ; H = 2·4.

$C_{17}H_{11}O_3,FeCl_4$ requires C = 44·4 ; H = 2·4 per cent.

This anhydroferrichloride melts indistinctly at about 225°, and the solution in sulphuric acid shows an intense green fluorescence. It is very sparingly soluble even in boiling glacial acetic acid, but dissolves somewhat and without fluorescence in water.

7-*Hydroxy*-4′ : 5′-*dimethoxy*-2 : 3-*indenobenzopyranol* (1 : 4) *Anhydrohydrochloride*,



This substance may be prepared by the action of hot hydrochloric acid on 2′ : 4′-dihydroxy-5 : 6-dimethoxy-2-benzylidene-1-hydrindone in the manner already described in other similar cases (pp. 1104, 1105), or by the following direct process. *β*-Resorcylaldehyde (2 grams) and 5 : 6-dimethoxyhydrindone (3 grams) are dissolved in methyl alcohol (25 c.c.), the solution is heated to boiling, and a rapid stream of hydrogen chloride passed through the clear liquid. Dark red prisms separate in a few minutes, and the whole is then cooled, filtered, and the precipitate washed with methyl-alcoholic hydrochloric acid. The substance is dried on porous porcelain in the air, and then in a vacuum desiccator over sulphuric acid:

0·1268 gave 0·2910 CO_2 and 0·0550 H_2O. $C = 62·6$; $H = 4·8$.
0·1700 „ 0·0715 AgCl. $Cl = 10·3$.
$C_{18}H_{15}O_4Cl,H_2O$ requires $C = 62·1$; $H = 4·9$; $Cl = 10·2$ per cent.

This hydrochloride darkens above 200°, and crystallises from methyl-alcoholic hydrochloric acid in deep crimson prisms or short needles.

It dissolves in sulphuric acid, yielding a yellow solution, which has a green fluorescence, and the dilute aqueous solution also fluoresces.

When sodium acetate is added to the solution of the hydrochloride, the base separates as a red, amorphous precipitate, which dissolves in alkalis and especially in ammonia, yielding beautiful deep red solutions.

The *platinichloride* is obtained as a pale orange precipitate by adding platinic chloride to the hot solution of the hydrochloride.

It was collected, washed with dilute hydrochloric acid, and dried in a vacuum over sulphuric acid:

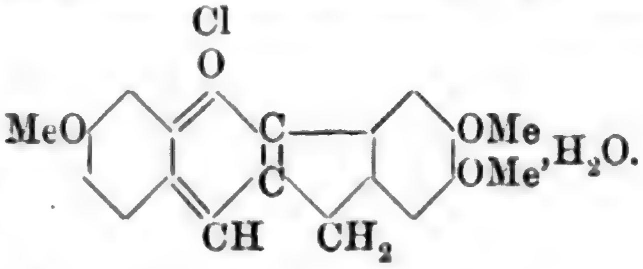
0·1211 gave 0·1884 CO_2 and 0·0375 H_2O. $C = 42·4$; $H = 3·4$.
$(C_{18}H_{15}O_4Cl)_2PtCl_4,2H_2O$ requires $C = 41·9$; $H = 3·3$ per cent.

The *anhydroferrichloride*.—When ferric chloride is added in excess to a solution of the hydrochloride in hot dilute hydrochloric acid, a yellowish-brown precipitate is produced, which is collected, washed with acetic acid, and crystallised from much acetic acid, from which it separates as a dark brown, crystalline powder with a strong green metallic lustre. For analysis, it was dried at 100°:

0·1102 gave 0·1782 CO_2 and 0·0310 H_2O. $C = 44·1$; $H = 3·1$.
$C_{18}H_{15}O_4,FeCl_4$ requires $C = 43·8$; $H = 3·1$ per cent.

This anhydroferrichloride is sparingly soluble in water and even in boiling glacial acetic acid.

4′ : 5′ : 7-*Trimethoxy*-2 : 3-*indenobenzopyranol* (1 : 4) *Anhydrohydrochloride*,



This substance, which interested us specially on account of its close relationship to the formula for trimethylbrazilin discussed in a previous paper (Trans., 1907, **91**, 1074), may be prepared as follows.

p-Methoxysalicylaldehyde (4 grams) and dimethoxyhydrindone (6 grams) are dissolved in methyl alcohol (50 c.c.), and the solution boiled by passing a rapid stream of hydrogen chloride. The solution becomes orange-brown, and the pyranol salt crystallises out as a deep orange powder. When this stage is reached, the stream of gas is stopped, and the liquid cooled and filtered. The residue is then recrystallised from methyl alcohol containing hydrochloric acid and dried in a vacuum over sulphuric acid:

0·1143 gave 0·2619 CO_2 and 0·0537 H_2O. C = 62·5; H = 5·2.
0·3238 „ 0·1344 AgCl. Cl = 10·1.
$C_{19}H_{17}O_4Cl,H_2O$ requires C = 62·9; H = 5·2; Cl = 9·8 per cent.

This hydrochloride darkens at about 175°, and, when rapidly crystallised from water, it separates as an orange-red, crystalline mass of very characteristic appearance, which differs entirely from that of the dimethoxy-derivative described in this paper. Under the microscope, the mass is seen to consist of long threads.

It is soluble in water, and the solution, which has a yellowish-green fluorescence, is immediately precipitated by hydrochloric acid.

The solution of the substance in sulphuric acid exhibits a similar, but more intense, green fluorescence. When potassium iodide is added to the aqueous solution of the hydrochloride, a characteristic dark red precipitate of the iodide is obtained.

The *platinichloride* is obtained as a yellow precipitate when a solution of the hydrochloride in hot dilute hydrochloric acid is mixed with platinic chloride. For analysis, this double salt was dried in a vacuum over sulphuric acid:

0·1225 gave 0·0229 Pt. Pt = 18·7.
$(C_{19}H_{17}O_4Cl)PtCl_4,2H_2O$ requires Pt = 18·4 per cent.

The *anhydroferrichloride.*—When a concentrated strongly acid solution of ferric chloride is added to an alcoholic solution of the hydrochloride, an orange precipitate is formed, which is collected and recrystallised from glacial acetic acid. It is thus obtained in stout, bright red needles, which, after drying at 100°, gave on analysis:

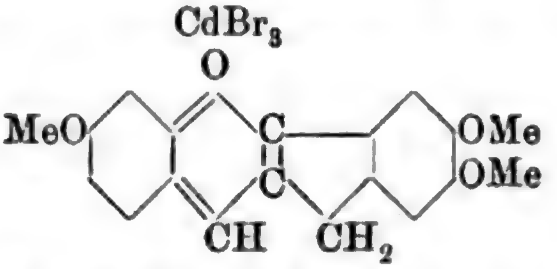
0·1207 gave 0·1980 CO_2 and 0·0370 H_2O. C = 44·7; H = 3·4.
$C_{19}H_{17}O_4,FeCl_4$ requires C = 45·1; H = 3·4 per cent.

This double salt melts at about 220° with some decomposition.

The *anhydrocadmium bromide.*—When a strong solution of cadmium bromide is added to a solution of the pyranol hydrochloride containing an excess of hydrobromic acid, a vermilion-red double salt separates, which is collected, washed with water, and dried in a vacuum over sulphuric acid:

0·1273 gave 0·1065 AgBr. Br = 35·6.
$C_{19}H_{17}O_4,CdBr_3$ requires Br = 36·3 per cent.

It is probable that the constitution of this characteristic and interesting double salt is that represented by the formula



Decomposition of the Pyranol by Hydrolysis.—In studying this decomposition, the pyranol hydrochloride (3 grams) dissolved in alcohol (50 c.c.) was digested with a strong solution of aqueous potassium hydroxide (5 grams) for four hours, water was then added, and the whole allowed to stand overnight. The filtered solution was acidified with acetic acid, the yellow precipitate collected, and acetylated with acetic anhydride and sodium acetate. The pale yellow needles of the acetyl compound, after crystallisation from alcohol, melted at 175°, and consisted of acetyl-2′-hydroxy-4′ : 5 : 6-trimethoxy-2-benzylidene-1-hydrindone, since when mixed with a specimen of this substance which had been prepared on a previous occasion (Trans., 1907, **91**, 1099) there was no alteration in melting point.

Conversion of Hydroxytrimethoxybenzylidenehydrindone into Trimethoxyindenobenzopyranol Anhydrohydrochloride by means of Hydrogen Chloride.—This interesting reaction was carried out in the manner described in the case of the corresponding reaction with salicylidenedimethoxyhydrindone (p. 1104), except that, as the unsaturated ketone hydrochloride in the present case is very sparingly soluble and changes with difficulty, a larger excess of methyl alcohol must be used and the hydrogen chloride passed for a longer time. An alternative method is to boil the substance with alcohol and hydrochloric acid in a reflux apparatus for several hours. In either case the product consists of the characteristic micro-threads, and shows all the reactions of trimethoxyindenobenzopyranol anhydrohydrochloride (p. 1107).

The compounds which follow have been prepared and investigated in conjunction with Mr. Maurice Russell Turner, B.Sc.

Resacetophenone Dimethyl Ether, $(MeO)_2C_6H_3 \cdot CO \cdot CH_3$ (2 : 4 : 1).

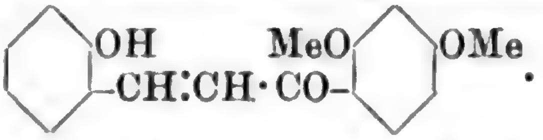
This substance has been prepared in small quantities by Tahara (*Ber.*, 1891, **24**, 2461) from pæonol by treatment with potassium hydroxide and methyl iodide. The methylation of resacetophenone with methyl sulphate and potassium hydroxide does not appear to have been described.

It may be advantageously carried out under the following conditions: Resacetophenone (180 grams) is dissolved in methyl alcohol (500 c.c.), mixed with a large excess of methyl sulphate (540 grams), and sufficient potassium hydroxide (40 per cent.) is slowly added to decompose all the methyl sulphate and to keep the liquid always strongly alkaline; the flask is heated on the water-bath for half an hour and then cooled. The product is extracted with ether, the ethereal solution washed with water, dried, evaporated, and distilled under the ordinary pressure:

0·1354 gave 0·3296 CO_2 and 0·0837 H_2O. C = 66·4; H = 6·9.
$C_{10}H_{12}O_3$ requires C = 66·7; H = 6·7 per cent.

Resacetophenone dimethyl ether distils without decomposition at 288°, and when crystallised from methyl alcohol melts at 40°.

2-*Hydroxy*-2′ : 4′-*dimethoxybenzylideneacetophenone*,



This unsaturated ketone is readily obtained by the condensation of salicylaldehyde with resacetophenone dimethyl ether in the presence of alkali. Salicylaldehyde (60 grams) and resacetophenone dimethyl ether (78 grams) are dissolved in methyl alcohol (50 c.c.), and potassium hydroxide (250 c.c. of 20%) added. The solution is heated almost to boiling and allowed to stand overnight, when a very bulky, red precipitate of the potassium derivative of the condensation product separates and almost fills the liquid.

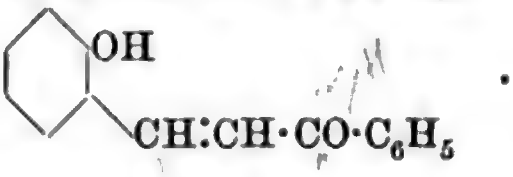
This is collected, drained on porous porcelain, dissolved in water, and the filtered solution poured into 20 per cent. potassium hydroxide, when the potassium derivative separates in a much purer condition. It is again collected, dissolved in a large quantity of water, and acidified with acetic acid. The yellow, oily precipitate which first separates gradually becomes crystalline, and, after crystallisation from alcohol, it is obtained in small, yellow needles or prisms melting at 124°:

0·1420 gave 0·3723 CO_2 and 0·0742 H_2O. C = 71·5; H = 5·8.
$C_{17}H_{16}O_4$ requires C = 71·8; H = 5·6 per cent.

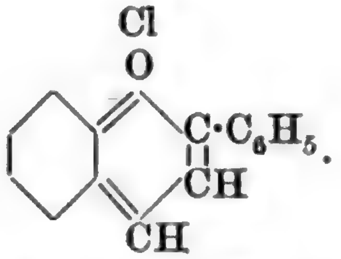
The characteristic *potassium* derivative separates from dilute potassium hydroxide in orange-red crystals:

0·3214 gave 0·0867 K_2SO_4. K = 12·1.
$C_{17}H_{15}O_4K$ requires K = 12·1 per cent.

The Action of Hydrochloric Acid on 2-Hydroxybenzylideneacetophenone,



The action of hydrochloric acid on this ketone leads, under the following conditions, to the formation of 2-phenylbenzopyranol anhydrohydrochloride,



The ketone is dissolved in acetic acid and boiled with concentrated hydrochloric acid for a few minutes and until a portion when diluted with water gives a clear solution of the oxonium hydrochloride. On account of its solubility, no attempt was made to isolate this hydrochloride, but its presence in the solution was demonstrated by the preparation and analysis of the *platinichloride.*

This salt separates on the addition of platinic chloride as a yellow, crystalline mass, which crystallises from a large quantity of dilute hydrochloric acid in orange prisms. For analysis, it was dried at 100°:

0·5039 gave 0·1195 Pt. Pt = 23·7.
0·2600 „ 0·0615 Pt. Pt = 23·7.
$(C_{15}H_{11}OCl)_2PtCl_4$ requires Pt = 23·7 per cent.

When a trace of this platini-salt (or a few drops of the solution of the oxonium hydrochloride) is added to concentrated sulphuric acid, a pale yellow solution is obtained, which exhibits a pure blue fluorescence much less intense, however, than that shown by the corresponding indeno-derivative (p. 1099).*

When dry hydrogen chloride is passed into a solution of 2-hydroxybenzylideneacetophenone in dry ether in the cold for three hours, the reaction proceeds differently, and a yellow substance separates in needles. This substance is very hygroscopic, and readily decomposes in the air. It was separated by filtration in dry air in a special apparatus, washed with dry ether, quickly transferred to a desiccator, and dried over sulphuric acid in a vacuum:

---

* The solution of all methoxyanhydropyranols in sulphuric acid fluoresce with various shades of green, and the blue fluorescence of the above solution is evidently due to the absence of methoxy-groups. We propose to study the influence of other groups on the character of fluorescence, as the results will probably have an important bearing on the problem of the conditions which cause and modify fluorescence.

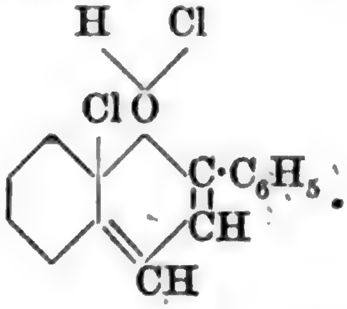
0·1003 gave 0·2217 CO_2 and 0·0439 H_2O. C = 60·3 ; H = 4·8.
0·1933 „ 0·1850 AgCl. Cl = 23·6.
$C_{15}H_{12}OCl_2,H_2O$ requires C = 60·6 ; H = 4·7 ; Cl = 23·9 per cent.

This *dichloride* * softens at 78° and melts at 85° with decomposition, and dissolves in sulphuric acid with a pure blue fluorescence.

When treated with water it dissolves, and platinic chloride precipitates the platinichloride of 2-phenylbenzopyranol (1 : 4).

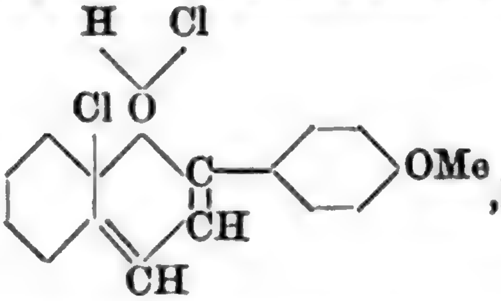
Sodium carbonate precipitates a yellow base, which is insoluble in alkalis.

It is pointed out in the introduction that the constitution of this dichloride is probably represented by the formula



.

The Hydrochloride of 4′-Methoxy-2-phenylbenzopyranol (1 : 4) *Anhydrochloride,*



,H_2O.

This dichloride is obtained when 2-hydroxy-4′-methoxybenzylideneacetophenone (Kostanecki and Zwayer, *Ber.*, 1908, **41**, 1337) is treated with hydrogen chloride under the following conditions. The well-cooled ethereal solution of the unsaturated ketone is saturated with hydrogen chloride, when the pale yellow solution rapidly becomes orange, and in about fifteen to twenty minutes the orange-red hydrochloride separates in needles. The crystals were filtered in an apparatus which avoids exposure to moisture, washed with ether, and dried over sulphuric acid in a vacuum :

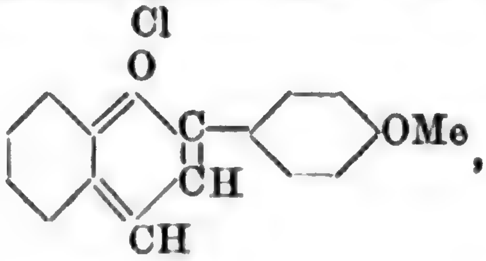
0·0987 gave 0·2139 CO_2 and 0·0478 H_2O. C = 59·1 ; H = 5·4.
0·1784 „ 0·1541 AgCl. Cl = 21·3.
$C_{16}H_{14}O_2Cl_2,H_2O$ requires C = 58·7 ; H = 5·0 ; Cl = 21·5 per cent.

This *dichloride* melts at 126° with decomposition, and is less affected by moisture than the dichloride described in the last section.

---

* Decker and von Fellenberg (*Annalen*, 1907, **356**, 302) evidently had this dichloride in their hands, but they did not analyse it, and erroneously describe it as having the composition $C_{15}H_{11}OCl$.

4′-Methoxy-2-phenylbenzopyranol (1 : 4) *Anhydrohydrochloride,*



, and its Double Salts.

The substance $C_{16}H_{14}O_2Cl_2,H_2O$, described in the last section, dissolves in water, yielding an orange solution, which, on standing, deposits orange crystals. These were collected, dried on porous porcelain in the air, and analysed, with the following results:

0·1233 gave 0·2414 CO_2 and 0·0661 H_2O. C = 53·4; H = 6·0.
0·1019 „ 0·2003 CO_2 „ 0·0558 H_2O. C = 53·6; H = 6·1.
0·2055 „ 0·0777 AgCl. Cl = 9·3.
$C_{16}H_{13}O_2Cl,5H_2O$ requires C = 53·0; H = 6·3; Cl = 9·7 per cent.

This *anhydrohydrochloride* melts at 87°, and may also be prepared by the action of hydrochloric acid on the solution of 2-hydroxy-4′-methoxybenzylideneacetophenone in boiling acetic acid, from which it separates, on dilution and long standing, in orange crystals.

The *anhydroplatinichloride.*—The aqueous solution of the hydrochloride gives a yellow precipitate with platinic chloride, which is collected and recrystallised from hot dilute hydrochloric acid. The orange-red crystals, dried at 100°, yielded:

0·2531 gave 0·0557 Pt. Pt = 22·0.
0·1814 „ 0·0399 Pt. Pt = 22·0.
$(C_{16}H_{13}O_2Cl)_2PtCl_4$ requires Pt = 22·1 per cent.

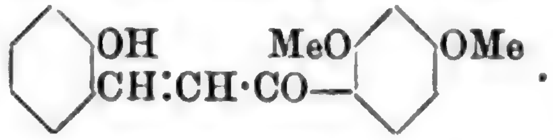
The *anhydroferrichloride.*—When a solution of the hydrochloride is mixed with concentrated ferric chloride, a yellow precipitate is obtained, which separates from acetic acid in yellow needles melting at 156°. For analysis, the substance was dried at 100°:

0·1654 gave 0·2668 CO_2 and 0·0484 H_2O. C = 44·0; H = 3·3.
0·3718 „ 0·0681 Fe_2O_3. Fe = 12·8
$C_{16}H_{13}O_2,FeCl_4$ requires C = 44·1; H = 3·0; Fe = 12·9 per cent.

A very interesting method of formation of this anhydroferrichloride from the unsaturated ketone is the following.

2-Hydroxy-4′-methoxybenzylideneacetophenone is dissolved in acetic acid, and a very concentrated solution of ferric chloride in hydrochloric acid is added. An excess of hydrochloric acid now precipitates a red compound, which is decomposed by water with formation of the unsaturated ketone, and the constitution of which is discussed on p. 1093. When it is dissolved in boiling acetic acid, the colour of the solution changes from red to yellow, and the ferrichloride described above crystallises in needles melting at 154—155°.

The Action of Hydrochloric Acid on 2-Hydroxy-2′ : 4′-dimethoxybenzylideneacetophenone,



The *hydrochloride* of this unsaturated ketone (p. 1109) is readily obtained when a solution of the ketone in acetic acid is saturated with hydrogen chloride in the cold, and separates in red crystals, but, owing to its susceptibility to moisture, we were unable to obtain accurate results on analysis. The percentage of chlorine was always somewhat less than that required for a hydrochloride, $C_{17}H_{16}O_4,HCl$. The *sulphate* gradually separates as a similar red substance when a drop of sulphuric acid is added to the solution of the unsaturated ketone in acetic acid. These substances are obviously analogously constituted to the salts of unsaturated ketones, which are described in our former paper (compare Trans., 1907, **91**, 1093).

Although the hydrochloride and sulphate could not be accurately analysed, the ferrichloride hydrochloride can be readily prepared pure and dry.

It is obtained when the unsaturated ketone, dissolved in acetic acid, is mixed with a concentrated solution of ferric chloride in hydrochloric acid. The brilliant red, crystalline precipitate which separates is collected, washed with a little glacial acetic acid, and dried at 50—60°:

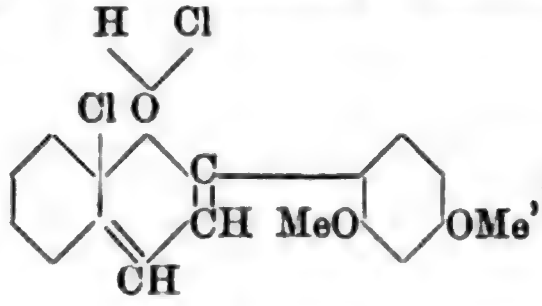
0·1749 gave 0·2525 CO_2 and 0·0571 H_2O. $C = 39·4$; $H = 3·6$.
0·1477 „ 0·2137 CO_2 „ 0·0490 H_2O. $C = 39·5$; $H = 3·7$.
0·2140 „ 0·3100 AgCl. $Cl = 35·4$.
$C_{17}H_{17}O_4,FeCl_4,HCl$ requires $C = 39·5$; $H = 3·5$; $Cl = 34·2$ per cent.

This interesting substance melts with decomposition at 178°, and is decomposed by water with separation of 2-hydroxy-2′ : 4′-dimethoxybenzylideneacetophenone. Small quantities may be recrystallised from acetic acid if the operation is quickly conducted, but when boiled with acetic acid for a few minutes it loses water and hydrogen chloride, and is converted into the anhydroferrichloride of 2′ : 4′-dimethoxy-2-phenylbenzopyranol (m. p. 188° : see p. 1114).

This behaviour is not only characteristic, but also of considerable interest.

The Hydrochloride of 2′ : 4′-Dimethoxy-2-phenylbenzopyranol

Anhydrohydrochloride,



,$2H_2O$.

This substance is obtained when 2-hydroxy-2′ : 4′-dimethoxybenzylideneacetophenone is heated with concentrated hydrochloric acid on the water-bath. The red hydrochloride first formed gradually dissolves, and a clear orange-yellow solution is produced, which, on cooling and stirring, deposits crystals. These are collected, recrystallised from concentrated hydrochloric acid, and dried on porous porcelain over sulphuric acid in a vacuum.

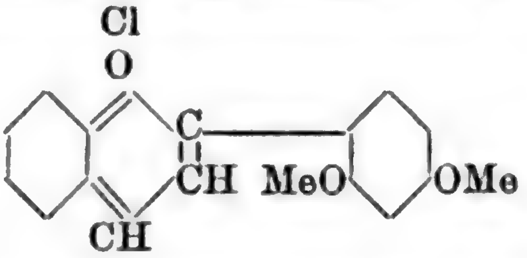
0·1357 gave 0·2693 CO_2 and 0·0674 H_2O. C = 54·1 ; H = 5·5.

0·2281 „ 0·1766 AgCl. Cl = 19·1.

$C_{17}H_{16}O_3Cl_2,2H_2O$ requires C = 54·4 ; H = 5·4 ; Cl = 18·9 per cent.

This substance consists of microscopic, deep orange-red needles, it melts with decomposition at 116°, and is very soluble in water or alcohol. When dilute alkali or sodium acetate is added to the aqueous solution, a pale yellow, amorphous base is precipitated which is free from chlorine.

Double Salts of 2′ : 4′-Dimethoxy-2-phenylbenzopyranol (1 : 4) *Anhydrohydrochloride,*



.

The *platinichloride.*—When the solution, obtained by dissolving the dichloride, $C_{17}H_{16}O_3Cl_2,2H_2O$ (see the last section) in water, is mixed with a solution of platinic chloride, a yellowish-orange double salt is precipitated, and may be crystallised from much dilute hydrochloric acid. Its colour was thereby deepened, and the red salt which separates after drying at 100° was found to decompose at about 230° :

0·1062 gave 0·1700 CO_2 and 0·0333 H_2O. C = 43·7 ; H = 3·5.

0·4666 „ 0·0970 Pt. Pt = 20·8.

0·3888 „ 0·0802 Pt. Pt = 20·6.

$(C_{17}H_{15}O_3Cl)_2PtCl_4$ requires C = 43·4 ; H = 3·2 ; Pt = 20·7 per cent.

The ferrichloride.—This substance may be prepared, as already mentioned (p. 1113), by boiling 2-hydroxy-2′ : 4-dimethoxybenzylideneacetophenone ferrichloride hydrochloride in acetic acid solution or by adding a concentrated solution of ferric chloride to a solution of the dichloride, $C_{17}H_{16}O_8Cl_2,2H_2O$, in dilute hydrochloric acid. In this latter case, a reddish-orange precipitate is formed, which is crystallised from acetic acid and dried at 100°:

0·1238 gave 0·1978 CO_2 and 0·0369 H_2O. C = 43·6; H = 3·3.
$C_{17}H_{15}O_8,FeCl_4$ requires C = 43·9; H = 3·2 per cent.

This *ferrichloride* crystallises in splendid red needles, which resemble chromic acid and melt at 189°. It dissolves moderately readily in water, a property which distinguishes it from the ferrichloride of the unsaturated ketone. The solution in sulphuric acid has a green fluorescence.

THE UNIVERSITY,
MANCHESTER.

CXI.—*Brazilin, Haematoxylin, and their Derivatives. Part IX.** *On Brazilein, Haematein, and their Derivatives.*

By PAUL ENGELS, WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON.

THE colouring matter brazilein is obtained when brazilin is treated with oxidising agents, and the change, due to the removal of two atoms of hydrogen,

$$\underset{\text{Brazilin.}}{C_{16}H_{14}O_5} + O = \underset{\text{Brazilein.}}{C_{16}H_{12}O_5} + H_2O,$$

is one of the most interesting and characteristic decompositions exhibited by brazilin.

Liebermann and Burg (*Ber.*, 1876, 9, 1886) first showed that a solution of brazilin in caustic alkalis rapidly acquires a magnificent cherry-red colour when it is exposed to air, and that the addition of acids then causes the precipitation of a reddish-violet, amorphous mass of crude brazilein. The same authors also showed that crystalline brazilein may be prepared from brazilin by oxidation in aqueous alcoholic solution with iodine, but the substance obtained in this way was found to contain about 1·3 per cent. of iodine.

---

* Part I, Trans., 1901, **79**, 1396; Parts II and III, Trans., 1902, **81**, 221, 235; Parts IV, V, and VI, Trans., 1902, **81**, 1008, 1040, 1057; Part VII, Trans., 1907, **91**, 1073; Part VIII, Trans., 1908, **93**, 489.

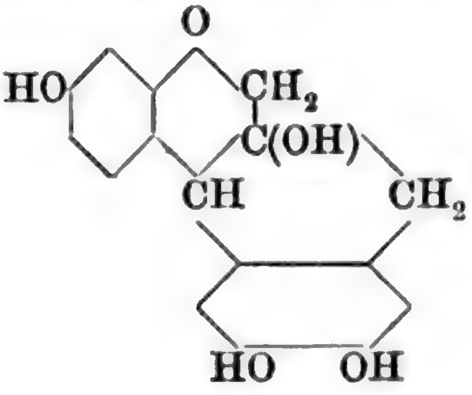
Pure brazilein was first prepared by J. J. Hummel and A. G. Perkin (Trans., 1882, **41**, 373) by passing air through a solution of brazilin in dilute ammonia, and was thus obtained in minute dark crystals having a grey metallic lustre and dissolving in alkalis with a brilliant red colour. The careful analyses of these authors showed that crystalline brazilein, dried at 100°, has the formula $C_{16}H_{12}O_5,H_2O$, and that, when heated at 130—140°, it loses the additional molecule of water.

The same authors also prepared pure hæmatein by passing air through a dilute ammoniacal solution of hæmatoxylin, $C_{16}H_{14}O_6$, and showed that it had the composition $C_{16}H_{12}O_6$. Buchka and Erck (*Ber.*, 1885, **18**, 1142) subsequently made the observation that crystalline brazilein may be obtained by oxidising brazilin in ethereal alcoholic solution with nitric acid, and they confirm the observation of Hummel and Perkin that, when dried at 100°, brazilein contains water, and that, when dried at 130°, the formula is $C_{16}H_{12}O_5$. Although a large number of experiments have been made with brazilein by different investigators, very few derivatives of importance have been prepared. Schall and Drall (*Ber.*, 1890, **23**, 1434 ; compare Herzig, *Monatsh.*, 1898, **19**, 743) prepared a crystalline triacetyl compound, $C_{16}H_9O_5(C_2H_3O)_3$, by digesting brazilein with acetic anhydride, zinc chloride, and zinc dust, but this substance can hardly be a derivative of brazilein. The same investigators also describe an amorphous oxime, $C_{16}H_{12}O_3(N{\cdot}OH)_2$, obtained by heating brazilein with hydroxylamine hydrochloride, alcohol, and hydrochloric acid in a sealed tube at 130°, and also an amorphous phenylhydrazine derivative of doubtful composition. Several bromo-derivatives of brazilein were also prepared by Schall and Drall, but these do not call for special mention. The methylation of brazilein has been attempted by Herzig (*Monatsh.*, 1898, **19**, 742), who heated brazilein with potassium hydroxide and methyl iodide, and obtained a syrupy substance insoluble in alkali, which yielded an amorphous acetyl derivative. On the assumption that the syrupy substance was trimethylbrazilein, Herzig assigns the formula $C_{16}H_8O(OMe)_3{\cdot}OAc$ to the amorphous acetyl compound. Since, however, it is shown in the present communication (p. 1117) that trimethylbrazilein is a beautifully crystalline substance, and does not yield an acetyl derivative, the substances prepared by Herzig cannot have the constitutions which he assigns to them.

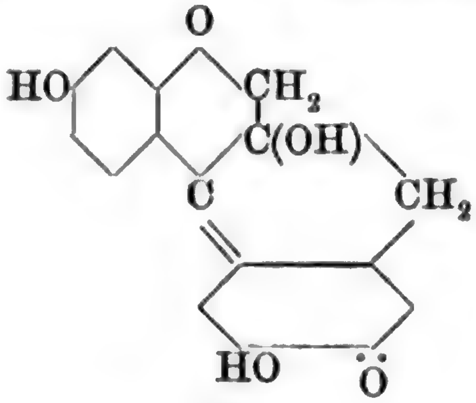
Perhaps the most characteristic property of brazilein (and also of hæmatein) is the formation of a very remarkable series of salts when these substances are treated with concentrated mineral acids.

This behaviour, which was first observed by J. J. Hummel and A. G. Perkin (Trans., 1882, **41**, 374), has been carefully investigated, and is discussed in detail in the present communication (p. 1121).

In Part VIII of this research (Trans., 1908, **93**, 496) it is clearly demonstrated that brazilin is represented by the constitutional formula (I), and it is pointed out that brazilein, derived from brazilin by the removal of two atoms of hydrogen, doubtless has the constitution (II).



(I.)

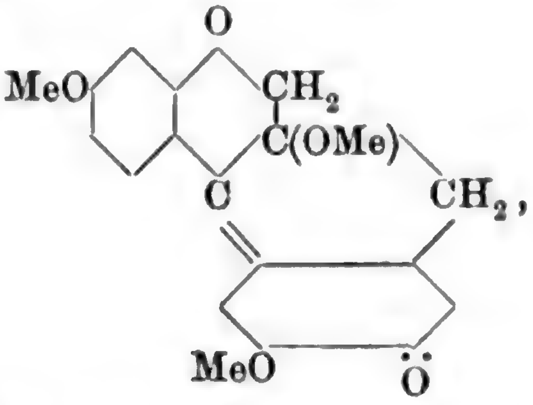


(II.)

During the course of the present investigation, many new derivatives and decomposition products of brazilein are described, the formation and properties of which can, without exception, be explained with the aid of the above formula. In investigating brazilein, we have proceeded on the lines which were so successful in the case of brazilin itself, that is to say, we first protected the hydroxy-groups by converting them into methoxy-groups before attempting to submit the molecule to the action of reagents.

Brazilin itself is readily methylated by treatment with methyl sulphate and potassium hydroxide, and practically the only product of the action is trimethylbrazilin (Trans., 1901, **79**, 1403). Brazilein, on the other hand, is methylated only with difficulty, and the product contains two highly important derivatives, *trimethylbrazilein* and *tetramethyldihydrobrazileinol*, together with large and varying quantities of mono- and di-methylbrazilein.

Trimethylbrazilein,

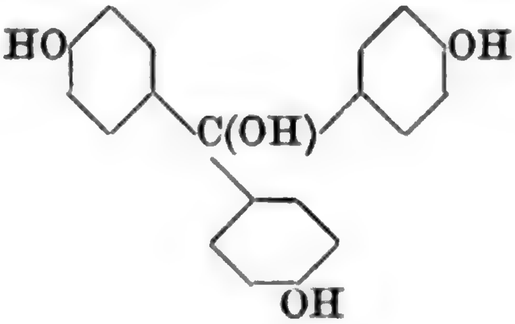


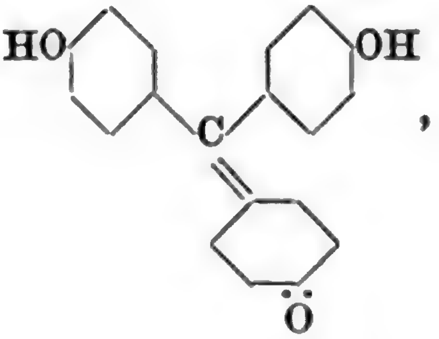
crystallises in magnificent amber prisms, melting at 177—178°, and yields with formic acid a highly characteristic formate, a splendid substance, which crystallises in brilliant ruby needles and is decomposed by alcohol or water into its constituents. It also combines with mineral acids to yield a series of highly characteristic salts and double salts, the constitution of which are discussed on p. 1121. One of the most striking properties of trimethylbrazilein is the fact that it dissolves in boiling dilute potassium hydroxide with addition of water and formation of trimethyldihydrobrazileinol,

$$\underset{\text{Trimethylbrazilein.}}{C_{16}H_9O_2(OMe)_3} + H_2O = \underset{\text{Trimethyldihydrobrazileinol.}}{C_{16}H_{10}O_2(OMe)_3{\cdot}OH.}$$

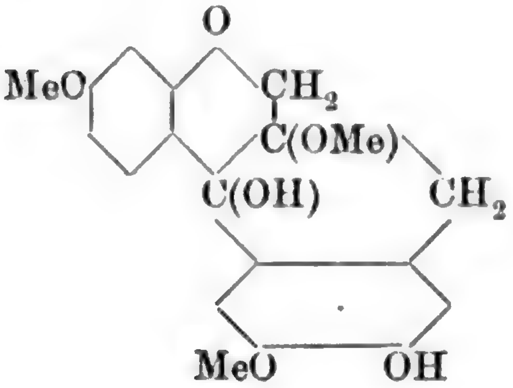
Trimethyldihydrobrazileinol crystallises in glistening, yellow prisms, melting at 177° with loss of water and formation of trimethylbrazilein. When it is boiled with acetic acid, it is converted quantitatively into the salt of trimethylbrazilein, which, on treatment with water, dissociates into trimethylbrazilein and acetic acid.

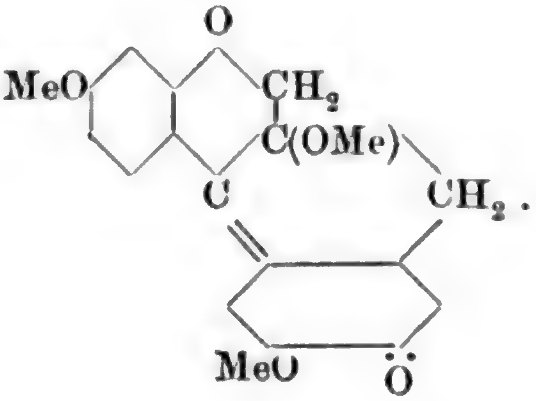
In these properties, trimethyldihydrobrazileinol shows a striking similarity to trihydroxytriphenylcarbinol, which readily loses water with formation of aurin, and, when treated with acids, is converted into salts of aurin,

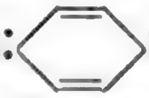




and there can be no doubt that the relationship between trimethyldihydrobrazileinol and trimethylbrazilein is a similar one, and is to be represented by the formulæ :



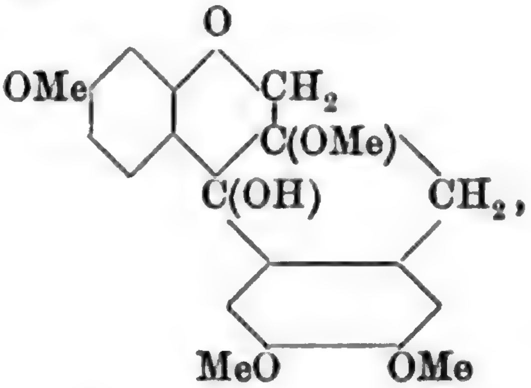


Another similar case is the formation of diphenylquinomethane, $(C_6H_5)_2C$::O, by the action of heat on *p*-hydroxytriphenylcarbinol (Bistrycki and Herbst, *Ber.*, 1903, **36**, 2335; Baeyer and Villiger, *ibid.*, 2774).

The interesting observation was also made that diphenylquinomethane, when boiled with potassium hydroxide, is converted by the addition of water to the quinone grouping into *p*-hydroxytriphenylcarbinol.

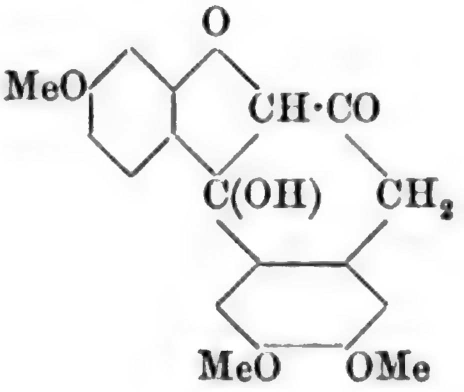
This change is obviously exactly analogous to the conversion of trimethylbrazilein into trimethyldihydrobrazileinol, and other examples of the reversible conversion of a quinone into the corresponding *p*-hydroxy-compound are to be found in a recent paper by Baeyer (*Annalen*, 1907, **354**, 152).

The second substance, which is produced in such large quantity, and is, indeed, frequently the principal product of the methylation of brazilein under the conditions employed in this research, is *tetramethyldihydrobrazileinol*,



a pale yellow, crystalline substance, which shows none of the extraordinary power of crystallising exhibited by trimethylbrazilein or trimethyldihydrobrazileinol. Its formation is due to the fact that, during the methylation of brazilein with methyl sulphate and potassium hydroxide, the excess of alkali, which is always present, converts much of the trimethylbrazilein formed into trimethyldihydrobrazileinol, which then itself undergoes methylation, and, in support of this explanation, we find that, when treated with methyl sulphate and potassium hydroxide, trimethyldihydrobrazileinol is readily converted into tetramethyldihydrobrazileinol.

In order to obtain additional evidence as to the constitution of this tetramethyl derivative, we have studied its behaviour on oxidation, and find that it is readily attacked by chromic acid with formation of a variety of substances (p. 1144). From the theoretical point of view, the most important product of oxidation is trimethylbrazilone,



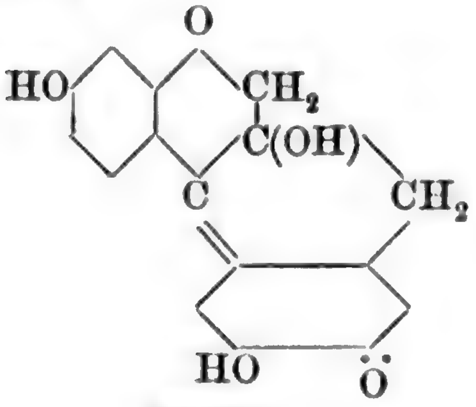
(compare Trans., 1908, **93**, 498), because the formation of this substance is not only valuable evidence of the constitution of tetramethyldihydrobrazileinol, but also makes it possible to control in an interesting manner some difficult points in connexion with the constitution of brazilin itself (p. 1129).

The colouring matter hæmatein closely resembles brazilein both in its method of formation and chemical behaviour. It is produced by the action of oxidising agents on hæmatoxylin, $C_{16}H_{14}O_6$, and is best prepared by passing air through a solution of hæmatoxylin in dilute ammonia and then precipitating with acetic acid (Hummel and Perkin, Trans., 1882, **41**, 368; Erdmann and Schultz, *Annalen*, 1882, **216**, 336).

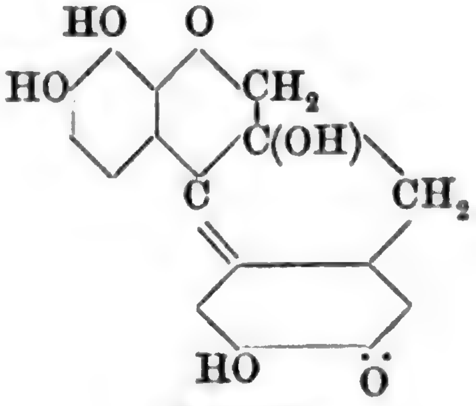
It crystallises in dark reddish-black plates with a brilliant metallic lustre, and dissolves in alkalis with an intense purple colour.

Hummel and Perkin have shown that the composition of hæmatein is $C_{16}H_{12}O_6$, and that, unlike brazilein, it crystallises without water of crystallisation.

It has long been assumed, and is clearly proved in the present investigation, that hæmatein is analogously constituted to brazilein. Hæmatein is, in fact, hydroxybrazilein, and the relationship of the two substances is at once evident from a comparison of their formulæ:



Brazilein.



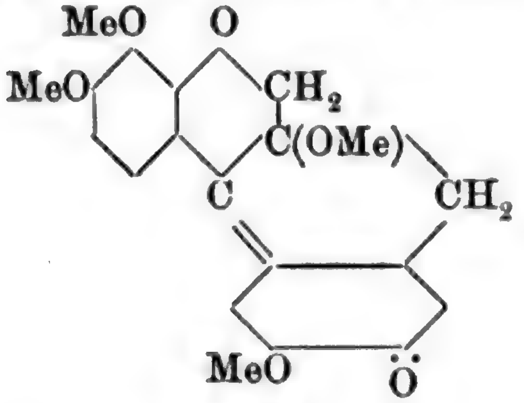
Hæmatein.

(compare Trans., 1908, **93**, 496). It is therefore not surprising that hæmatein should behave on methylation in a similar way to brazilein.

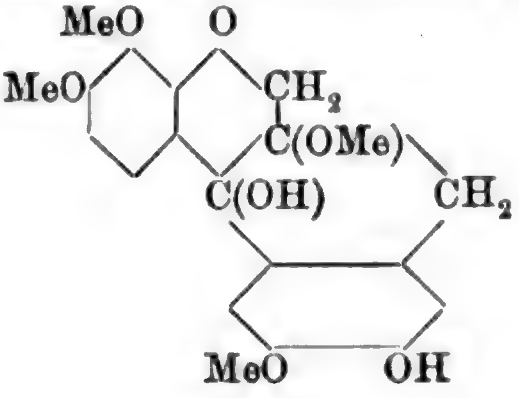
Unfortunately, however, the presence of the extra hydroxy-group enormously increases the difficulty of complete methylation, and this fact, taken in conjunction with the much greater solubility of the products, prevented us for a long time from isolating and examining these highly interesting methyl derivatives of hæmatein.

Subsequently we were able to overcome these difficulties, and the crude product of methylation which we finally obtained was found to consist essentially of tetramethylhæmatein and pentamethyldihydrohæmateinol.

Tetramethylhaematein (I) crystallises in splendid amber prisms, melts at 210°, and, when digested with dilute potassium hydroxide, is converted by the addition of water into *tetramethyldihydrohaemateinol* (II).



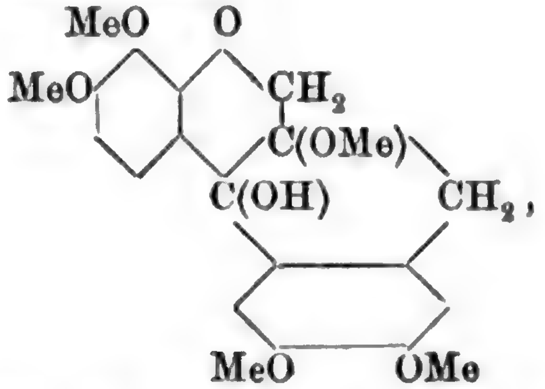
(I.)



(II.)

This substance crystallises in yellow prisms, melts at 183°, and is reconverted into tetramethylhæmatein by heat, or, better, by boiling with glacial acetic acid.

Pentamethyldihydrohaemateinol,



crystallises with great facility in pale yellow plates, melts at 160°, and is also produced when tetramethyldihydrohæmateinol is methylated with methyl sulphate in the presence of potassium hydroxide.

This brief description will suffice to show that brazilein and hæmatein behave in a similar manner, and give rise to exactly analogous products of methylation when they are subjected to the action of methyl sulphate and potassium hydroxide in large excess.

The Pyranol Salts derived from Brazilein, Haematein, and their Methyl Derivatives.

In the year 1882, J. J. Hummel and A. G. Perkin (Trans., **41**, 367) made the remarkable observation that brazilein, $C_{16}H_{12}O_5$, and hæmatein, $C_{16}H_{12}O_6$, are converted by the action of mineral acids into orange or red salts, from which it was not found possible by the action of alkalis to regenerate the original colouring matters.

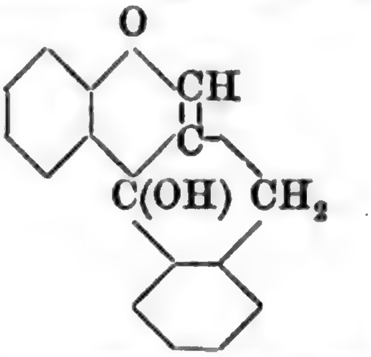
The sulphate obtained from brazilein is formed according to the equation

$$C_{16}H_{12}O_5 + H_2SO_4 = C_{16}H_{11}O_4{\cdot}HSO_4 + H_2O,$$

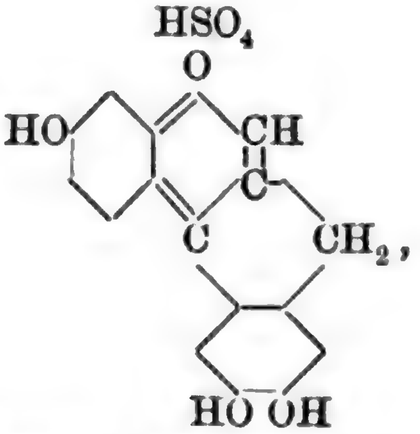
and was named *iso*brazilein acid sulphate. The chloride, $C_{16}H_{11}O_4{,}Cl$, a dark brown, crystalline substance with a violet lustre, is formed by the action of hydrochloric acid on brazilein, and the corresponding hydrobromide, $C_{16}H_{11}O_4,Br$, crystallises in deep orange prisms.

These salts were named *iso*brazilein chlorohydrin and bromohydrin respectively. Hæmatein yields an exactly similar series of orange or red *iso*hæmatein salts.

Whilst we were examining these highly coloured salts, we were much struck with the similarity they showed to the pyranol salts described by Bülow and Sicherer (*Ber.*, 1901, **34**, 3890), and this led us to undertake the investigation of a large number of pyranol salts in order to determine whether they were really analogously constituted to the *iso*brazilein and *iso*hæmatein salts (compare p. 1123). As the work proceeded, we became more and more convinced of the pyranol nature of these salts, and we have now no hesitation in formulating them all as derivatives of 4 : 3-indenobenzopyranol(1 : 4),

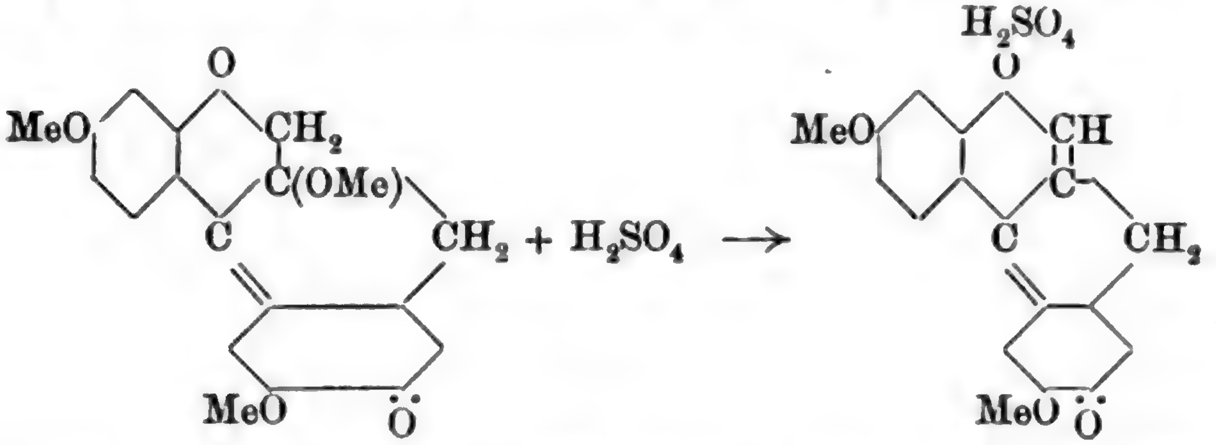


and to represent them as anhydro-salts in the manner suggested in the paper immediately preceding this. Thus *iso*brazilein acid sulphate has the constitution

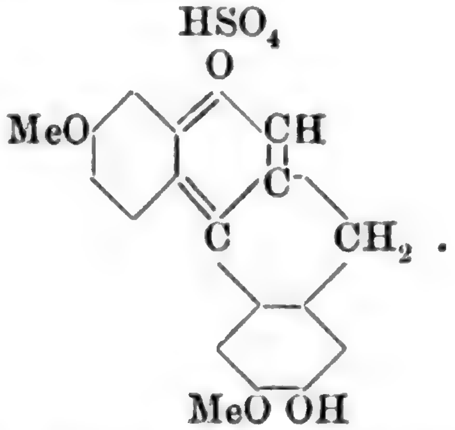


and is 7 : 4′ : 5′-*trihydroxy*-4 : 3-*indenobenzopyranol*(1 : 4) *anhydro-hydrogen sulphate*. *iso*Brazilein chlorohydrin has the analogous formula with Cl in the place of HSO_4, and the *iso*hæmatein salts are, of course, also similarly constituted.

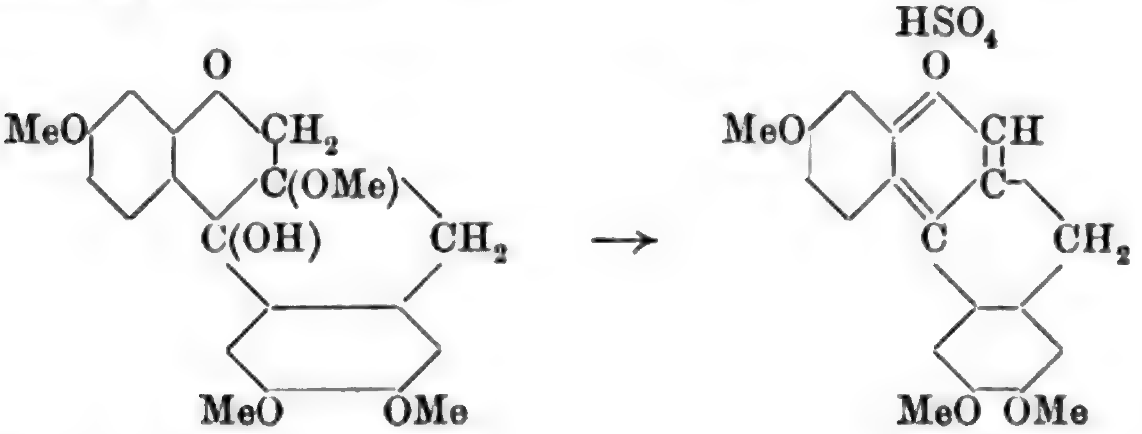
In order to obtain evidence in support of this view, we have studied the action of sulphuric acid on the methyl derivatives of brazilein and hæmatein, and also on tetramethyldihydrobrazileinol and pentamethyldihydrohæmateinol. In all these cases, oxonium sulphates were obtained which could be converted by the usual methods into other characteristic simple and double salts. The examination of these salts has proved beyond a doubt that they are closely connected with the 2 : 3-indenobenzopyranol anhydro-salts described in the communication immediately preceding this paper. One of the first cases investigated was that of the action of sulphuric acid on trimethylbrazilein, and this will serve as an example in illustration of the formation of all the other salts. The analysis of the sulphates shows clearly that methyl alcohol is eliminated during its formation, and the change which takes place is evidently the following :



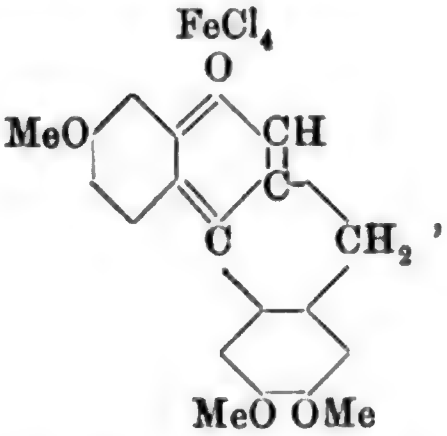
Since, however, the pyranol base is soluble in alkalis, the quinonoid oxygen must have become phenolic, and the correct formula for the sulphate is therefore in all probability



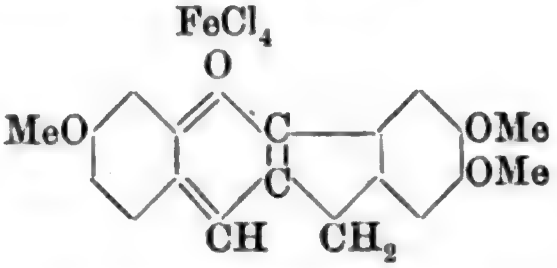
This formula not only accounts for all the properties of the salt and its derivatives, but also brings its constitution into harmony with that of the other sulphates, such as, for example, the sulphate obtained from tetramethyldihydrobrazileinol. In the case of this latter salt, the *p*-quinonoid grouping cannot be present, and the anhydro-salt must therefore be *o*-quinonoid :



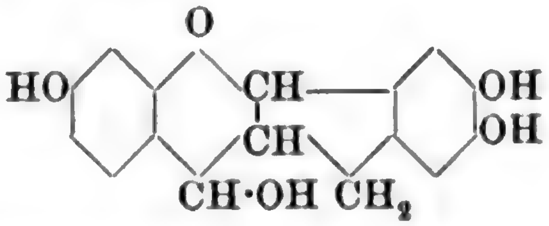
The *anhydroferrichloride* must therefore have the formula



and is isomeric with, and closely related to, the *anhydroferrichloride* of 4′ : 5′ : 7-*trimethoxy*-2 : 3-*indenobenzopyranol* (1 : 4),

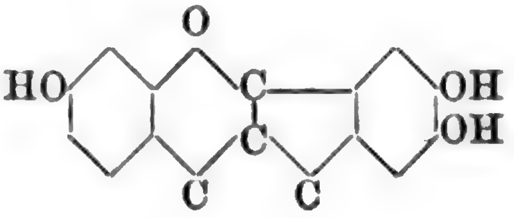


(compare p. 1107). The two substances are naturally quite distinct, but at the time when it was thought that the constitution of brazilin was represented by the formula



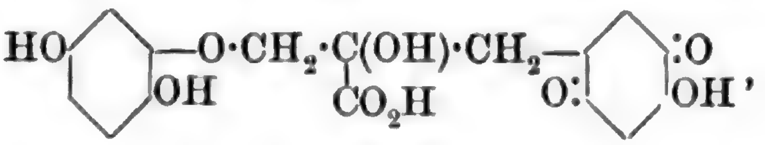
(Trans., 1908, **93**, 491), this point was of extraordinary interest.

Had this formula for brazilin been correct, the pyranol salts from tetramethyldihydrobrazileinol would have been identical with the corresponding salts of 4′ : 5′ : 7-trimethoxy-2 : 3-indenobenzopyranol (1 : 4). That this was found not to be the case was almost the first evidence of the incorrectness of any formula for brazilin based on the structure



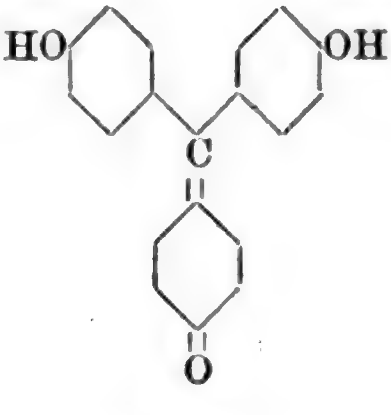
*The Action of Hydrogen Peroxide on Brazilein, Haematein, and their Derivatives.**

One of the most remarkable series of decompositions which brazilein, hæmatein, and their derivatives exhibit is the behaviour which these substances undergo when they are treated with hydrogen peroxide in acetic acid solution. Under these conditions, brazilein is converted into a deep brown, crystalline substance, which is obviously a quinone, and to which we have assigned the constitution

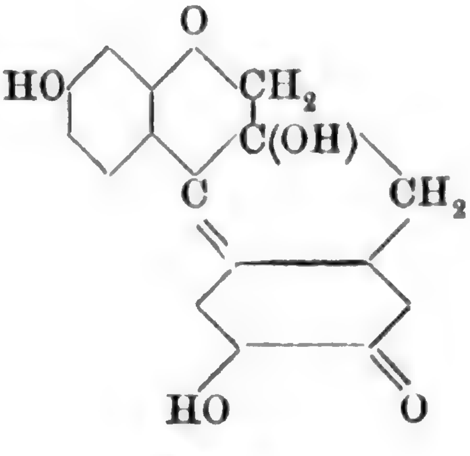


and the name *a*:4:2′:5′-*tetrahydroxy-β′-phenoxy-β*-2:5-*quinoyl*iso*butyric acid*. This interesting quinone is converted by reduction in alkaline or acid solution, into a colourless substance, and is characterised by the remarkable series of colour reactions which it exhibits (p. 1155). Its properties are so unusual that we propose to submit it to further detailed investigation.

For a considerable time, the nature of this quinone could not be understood, and the first clue to its formation was obtained as the result of a series of experiments on the action of hydrogen peroxide on aurin. It has already been suggested (p. 1118) that aurin and brazilein



Aurin.

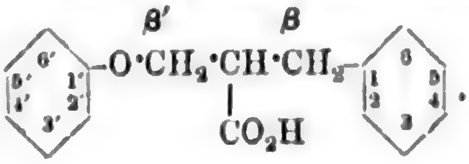


Brazilein.

are in many ways analogously constituted, and, in order to obtain some indication of the mechanism of the oxidation of brazilein and its derivatives by hydrogen peroxide, experiments were instituted

---

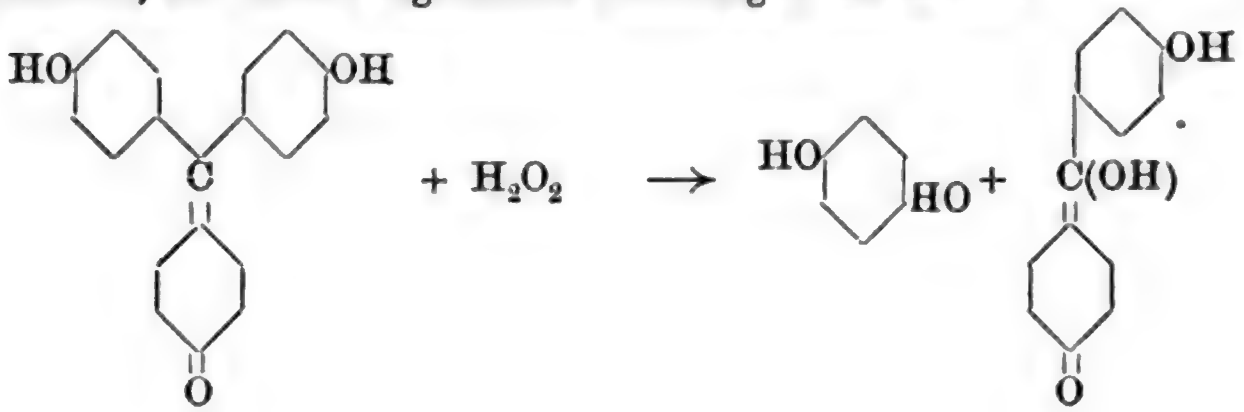
* In the scheme of nomenclature employed in this section, these substances are considered as derivatives of *β-phenyl-β′-phenoxyisobutyric acid*,



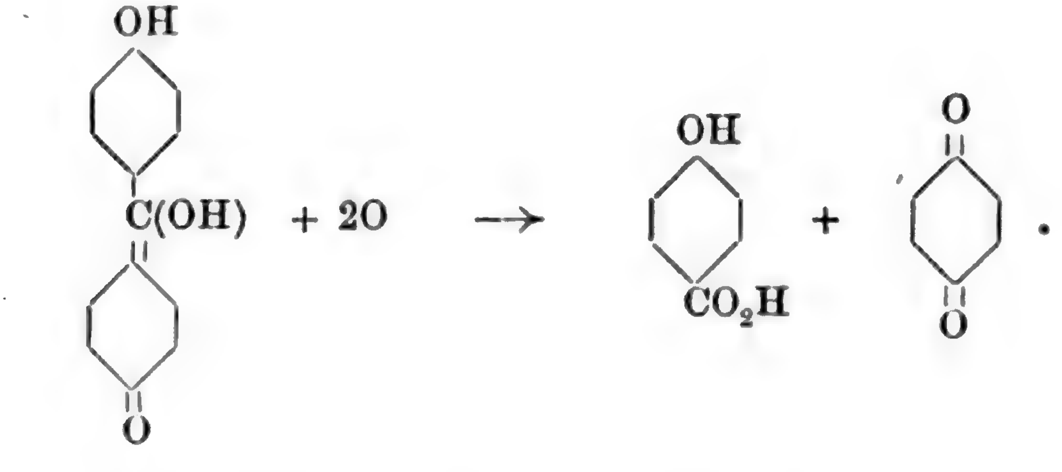
under the same conditions with aurin. A preliminary account of these experiments has been published (Perkin, Proc., 1907, **23**, 166), and it is there shown that aurin, when oxidised by hydrogen peroxide in acetic acid solution, yields *p*-hydroxybenzoic acid and quinone.

The probable course of this interesting decomposition (which seems to be shown by other quinonoid substances) is the following.

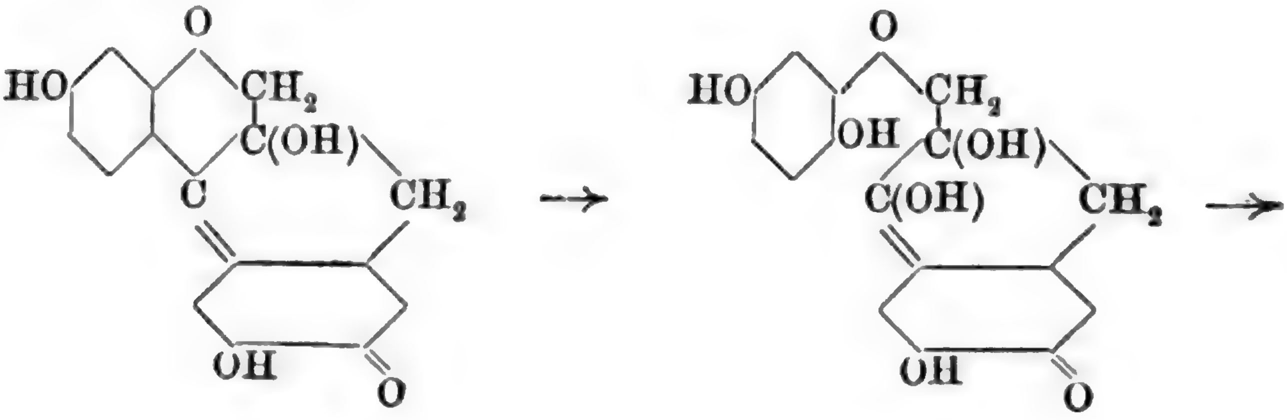
Aurin in the first place reacts with one molecule of hydrogen peroxide, and suffers degradation according to the scheme:

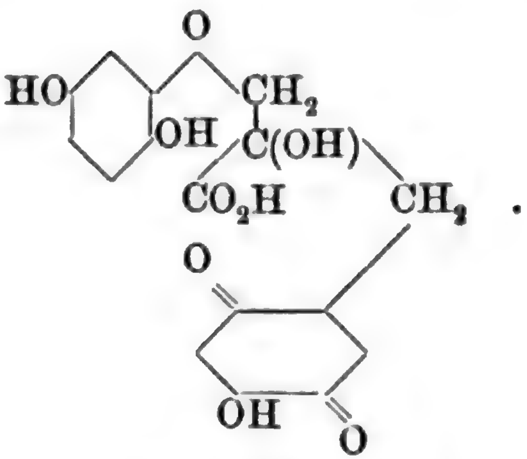


The latter substance, either as such or in its tautomeric form, is then further oxidised to *p*-hydroxybenzoic acid and benzoquinone

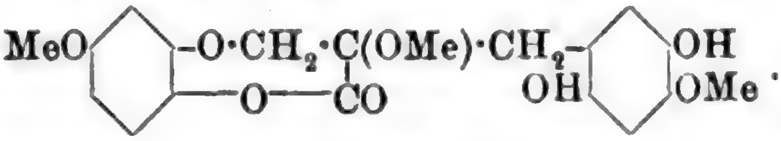


If an exactly analogous series of reactions is formulated in the case of brazilein, it is seen that the result of the addition of hydrogen peroxide and subsequent oxidation is the formula which we suggested for the quinone:

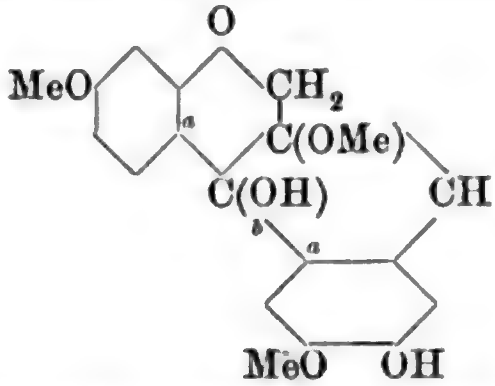




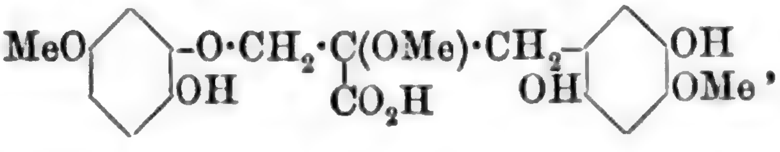
When *trimethylbrazilein* is treated with hydrogen peroxide in acetic acid solution, it behaves somewhat differently from brazilein, and is converted almost quantitatively into a colourless lactone, which melts at 218° and contains three methoxy-groups. The investigation of this substance clearly indicates that it is the lactone of *2′ : 2 : 5-trihydroxy-a : 4 : 5′-trimethoxy-β′-phenoxy-β-phenyl*iso*butyric acid*, and that its constitution is represented by the formula



The formation of this lactone from trimethylbrazilein can be explained on the lines adopted in the case of brazilein, but it is perhaps more readily understood if we consider the observation that the same lactone is produced even more readily by the action of hydrogen peroxide on trimethyldihydrobrazileinol (p. 1158):



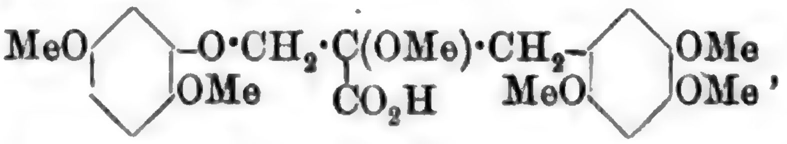
If two hydroxy-groups are added to (*a*, *a*,) and one oxygen atom to (*b*) in this formula, the following expression is obtained:



and the dehydrating action of the warm acetic acid employed causes elimination of water and formation of the lactone of melting point 218°. Since, however, the hydroxy-acid contains two hydroxyquinol residues, lactone formation may obviously take place between the carboxyl group and the hydroxyl group of either of these residues.

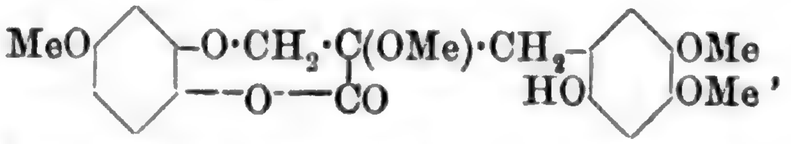
We think it probable that the hydroxy-group of the residue on the left hand takes part in the lactone formation principally because the lactone behaves towards oxidising agents as though it contained two free hydroxy-groups in the *p*-position, and we have therefore assigned to it the constitution given above.

When this lactone is methylated in strong alkaline solution with methyl sulphate, the lactone ring suffers disruption, and the product consists of the *methyl ester* of *a* : 2 : 4 : 5 : 2′ : 5′-*hexamethoxy-β′-phenoxy-β-phenyl*iso*butyric acid.* The free acid,



obtained from the methyl ester by hydrolysis, crystallises with one molecule of water in prisms and melts at 102°.

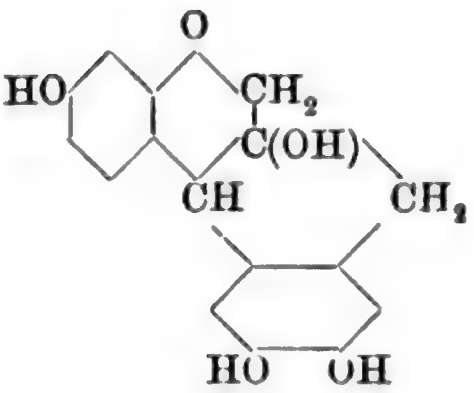
Tetramethyldihydrobrazileinol also reacts readily with hydrogen peroxide in acetic acid solution (p. 1161), and is converted into the lactone of 2′ : 2-*dihydroxy-a* : 4 : 5 : 5′-*tetramethoxy-β′-phenoxy-β-phenyl*iso-*butyric acid* (m. p. 160°):



a change which is exactly analogous to the formation of the lactone of melting point 218° from trimethylbrazilein under the same conditions. The lactone (m. p. 160°) yields on treatment with methyl sulphate and potassium hydroxide the methyl ester of *a* : 2 : 4 : 5 : 2′ : 5′-hexamethoxy-*β′*-phenoxy-*β*-phenyl*iso*butyric acid (see above), and this fact is strong evidence that the explanations of the formation of these lactones and the constitutional formulæ assigned to them are correct.

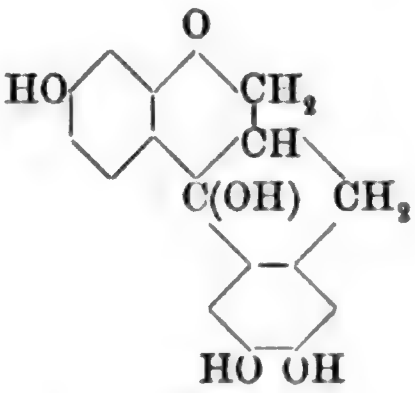
When hæmatein is treated with hydrogen peroxide under the conditions described in the case of brazilein, it yields a nearly black quinone, the investigation of which is not yet complete. The methyl derivatives of hæmatein also react readily with hydrogen peroxide, but the products are syrups and have, so far, not been obtained in a crystalline condition, and they could therefore not be purified and analysed.

In the foregoing pages, we have adopted the formula I (see p. 1129) for brazilin which was suggested in our last paper (Trans., 1908, **93**, 496), and have accepted it as correct. It was, however, pointed out at that time that the position of the alcoholic hydroxyl group in that formula was open to some doubt, and that there were, indeed, two formulæ for brazilin, namely,



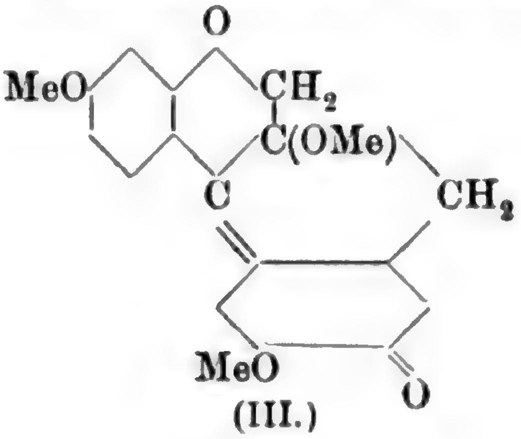
(I.)

and

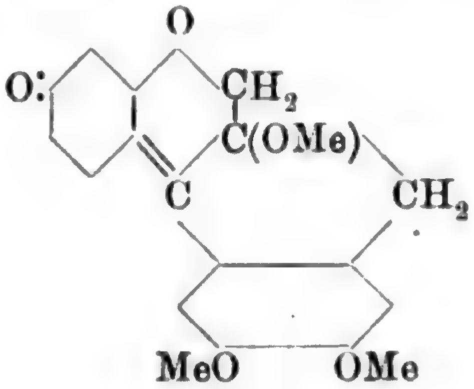


(II.)

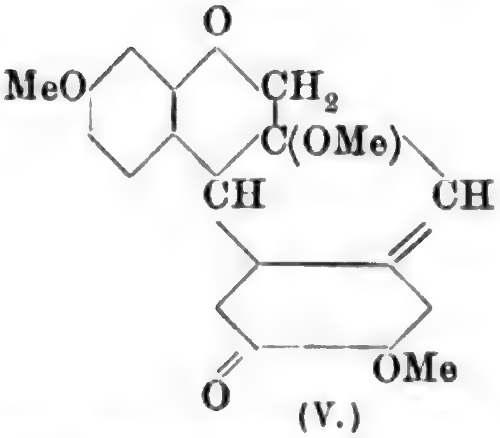
which seemed to account almost equally well for all the then known properties of this substance. The study of the methyl derivatives of brazilein, and especially the investigation of tetramethyldihydrobrazileinol, has now made it possible to decide definitely in favour of formula I. The two expressions (I and II) for brazilin lead to four possible formulæ for trimethylbrazilein, three of which (III, IV, and V) are derived from I and the other one, VI, from II:



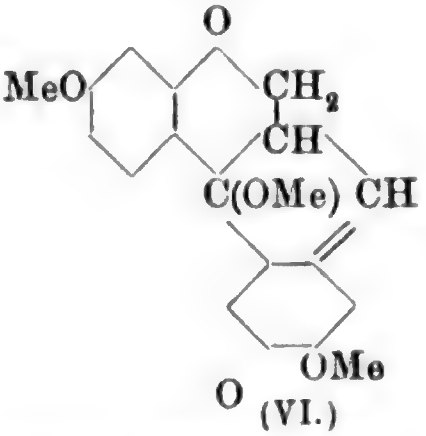
(III.)



(IV.)

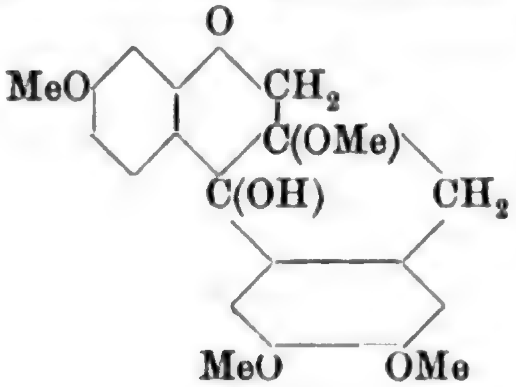


(V.)

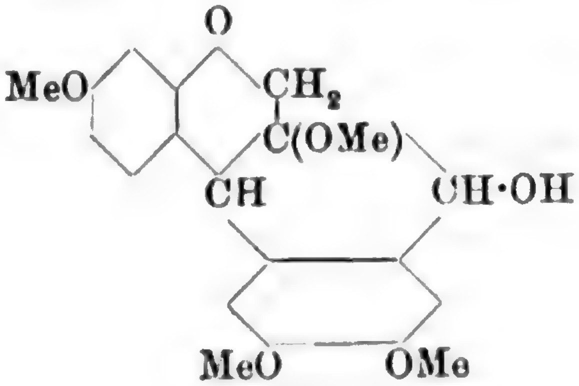


(VI.)

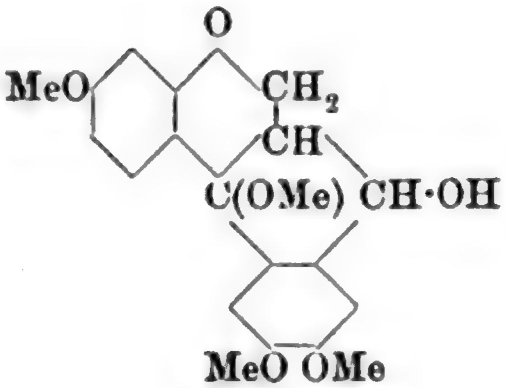
These four expressions for trimethylbrazilein lead to three formulæ for *tetramethyldihydrobrazileinol*, namely,



(VII.)

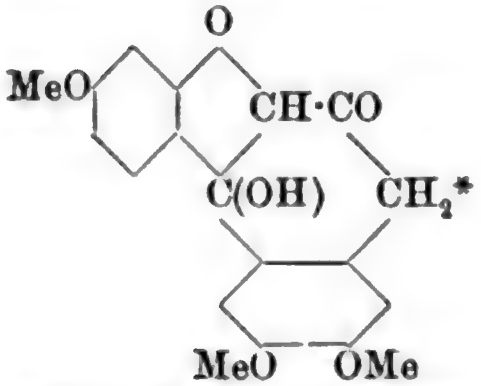


(VIII.)



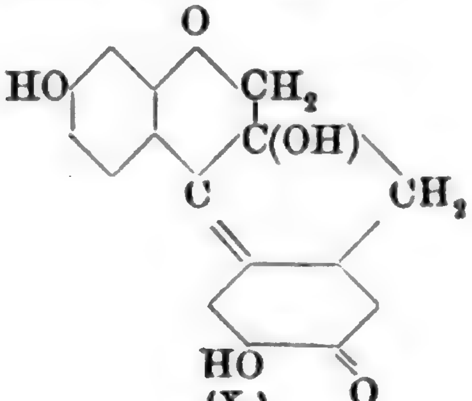
(IX.)

Since, however, tetramethyldihydrobrazileinol yields trimethylbrazilone,

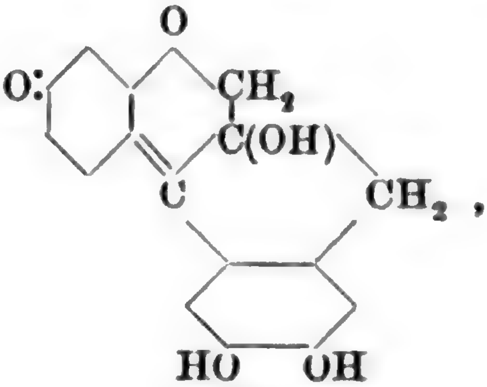


(*loc. cit.* p. 498), on oxidation, it follows that the correct expression for the former must contain a $>CH_2$ group in the position marked by the asterisk in the latter (compare Trans., 1908, **93**, 492). The only formula which fulfils this condition is VII, and this therefore must represent tetramethyldihydrobrazileinol. This expression may be derived from III or IV for trimethylbrazilein, and, as these are both derived from formula I, it follows that this expression, which we have adopted in this and in the last paper, must be the constitutional formula of brazilin. The question now arises "which of the formulæ III and IV represents trimethylbrazilein?" The results of our experiments on the methylation of brazilein have shown that there is one phenolic hydroxyl group in that substance which is exceedingly difficult to methylate, and, indeed, the fact that dimethylbrazilein (p. 1132) is one of the products of methylation and is soluble in dilute alkalis proves that the alcoholic hydroxyl group in brazilein is actually methylated before that particular phenolic hydroxyl group.

The formulæ for brazilein corresponding with III and IV for trimethylbrazilein are



(X.)



(XI.)

and it is clear that XI does not offer an explanation of this difficulty of methylation, since both the *o*-hydroxy-groups in the positions they occupy in that formula are well known to be readily methylated. On the other hand, formula X contains a hydroxy-group adjacent to the quinonoid oxygen, and it has been repeatedly observed that a hydroxy-group adjacent to an acidic group, such as $>CO$ or $-CO_2H$, or to quinonoid oxygen is methylated only with extreme difficulty. These and other arguments which will readily suggest themselves clearly prove, in our opinion, that the constitution of brazilein is represented by formula X and consequently that of trimethylbrazilein by III.

EXPERIMENTAL.

The Methylation of Brazilein.

The brazilein which we employed in the experiments described in this paper was prepared from brazilin by oxidation with iodine (compare Liebermann and Burg, *Ber.*, 1876, **9**, 1886; Benedict, *Annalen*, 1875, **178**, 101). The small quantity of iodine which it contained was removed during the process of conversion into trimethylbrazilein.

Brazilin (carefully purified by recrystallisation from dilute alcohol, 50 grams) is dissolved in the smallest possible quantity of warm alcohol, mixed with hot water (4 litres), the clear solution cooled to 60—70°, then a solution of iodine (33·8 grams) in alcohol (42·5 c.c.) added, and the mixture allowed to remain overnight.

The brazilein, which separates in characteristic glistening crystals, is collected, well washed, first with water and then with warm alcohol, and dried on porous porcelain at the ordinary temperature. The yield is about 30 grams.

The conversion into trimethylbrazilein is carried out as follows: Brazilein (115 grams) is mixed in a large, round-bottomed flask with water (550 c.c.) and ice (200 grams), aqueous potassium hydroxide (185 c.c. of 43 per cent.*) is then added, and the flask well shaken until the brazilin has completely dissolved. Methyl sulphate (210 c.c.) is then poured in all at once, and the whole continuously shaken, rise of temperature being carefully checked by cooling, when it will be observed that, after about forty to fifty minutes, a solid will have commenced to separate. A further quantity of the potassium hydroxide (130 c.c.) is now added in three or four portions during the course of a quarter of an hour, the shaking and cooling continued as before, and, when the operation is finished, the deep crimson colour of the original alkaline solution will have changed to brown.

After remaining for four hours, the precipitate is collected on calico on filter frames, ground with water, filtered at the pump, and washed with very dilute sodium hydroxide and then with water until the washings are only a pale sherry colour.*

---

* This corresponds approximately with equal quantities of potassium hydroxide (Merck) and water.

The ochreous residue, after drying on porous porcelain over sulphuric acid, should weigh about 80 grams. The deep reddish-brown filtrate is mixed with ice, just acidified with dilute sulphuric acid (or, better, acetic acid), and the orange precipitate collected, washed, and dried on porous porcelain. The residue may be crystallised from acetic acid, from which it separates as a garnet, crystalline mass, which is soluble in alkalis, and, on analysis, gives numbers agreeing approximately with those required for *dimethylbrazilein*:

0·1541 gave 0·3881 CO_2 and 0·0699 H_2O. C = 68·7; H = 5·0.

$C_{18}H_{16}O_5$ requires C = 69·2; H = 5·1 per cent.

The methoxy-groups were determined by Zeisel's method,† with the following result:

0·2251 gave 0·3163 AgI. OMe = 18·5.

$C_{18}H_{16}O_5$, containing two OMe groups, requires OMe = 19·7 per cent.

As the yield of crystalline substance was only very small, it has, in the meantime, not been further investigated. The crude dimethylbrazilein is, however, very valuable, and was always carefully collected and subjected to further methylation in the following way.

The dry substance (250 grams) is dissolved in water (1 litre) and potassium hydroxide solution (180 c.c. of 43 per cent.), mixed with methyl sulphate (216 c.c.), and the whole well shaken and cooled as before, when, in about twenty minutes, a precipitate will commence to separate.

A further quantity of potassium hydroxide (140 c.c.) is then added in small quantities at a time, and, after shaking and cooling for ten minutes, the whole is left overnight and the product worked up exactly as before. The total yield of the product of methylation, insoluble in dilute alkali, should be about 80 grams from the 115 grams of brazilein employed.

Separation of Trimethylbrazilein and Tetramethyldihydrobrazileinol.

The crude product of the methylation of brazilein, insoluble in alkali, consists essentially of a mixture of trimethylbrazilein and tetramethyldihydrobrazileinol in approximately equal quantities. The separation of these substances is a matter of considerable experimental difficulty, owing to the presence of resinous matter, and to the fact that tetramethyldihydrobrazileinol is so soluble in nearly all solvents, and has so little tendency to assume crystalline form, that it prevents the crystallisation of the trimethylbrazilein. Ultimately we devised the two following methods of separation, which have enabled us to prepare pure trimethylbrazilein in considerable quantities.

---

* When, as sometimes happens, the crude product is dark coloured, soft, and resinous, it is ground with very dilute sodium hydroxide and allowed to stand until it has become hard and granular.

† The determinations of methoxy-groups, given in this paper, were all carried out by Perkin's modification of Zeisel's method (Trans., 1903, **83**, 1367), which was found to be very rapid and accurate.

I. *Separation by Means of Formic Acid.*—The crude product (62 grams) is warmed with formic acid (100 c.c. of sp. gr. 1·22) at 50° until dissolved, warm water (35 c.c.) is then added, and the deep red solution left for several days. The brilliant crimson, crystalline sediment of trimethylbrazilein formate (p. 1136) is collected, washed with dilute formic acid (1 part to 4 parts of water), drained on porous porcelain, and boiled with dilute alcohol (75 per cent.). The alcohol decomposes the formate, and, on cooling, pure trimethylbrazilein separates in glistening, amber prisms, but the yield is usually very unsatisfactory. The tetramethyldihydrobrazileinol contained in the mother liquors may be precipitated by water and separated from trimethylbrazilein by treatment with alcoholic potash in the way described on p. 1138.

II. *Separation by Means of Ether.*—In dealing with large quantities of material, the following process of separation gives the more satisfactory results, and is based on the observation that, whilst tetramethyldihydrobrazileinol is very soluble in ether, trimethylbrazilein is sparingly soluble in this solvent. The crude product is kneaded with ether in a mortar, the ether being decanted and replaced by fresh solvent about fifteen to twenty times and until practically all the tetramethyldihydrobrazileinol has been extracted. The residue is then dissolved in boiling alcohol and allowed to stand for twenty-four hours, when a cake of crystalline trimethylbrazilein will have separated, and further large quantities may be obtained by digesting the mother liquor with animal charcoal and then allowing it to concentrate slowly in the air. The ethereal solution containing the tetramethyldihydrobrazileinol is evaporated, and the residual amber syrup kneaded and left in contact with water until it has been converted into a chalky mass, which is drained on porous porcelain and purified as explained on p. 1139.

Trimethylbrazilein, $C_{16}H_9O_2(OMe)_3$.

For analysis, the substance, obtained as described in the last section, was several times recrystallised from alcohol:

I. 0·2038 gave 0·5182 CO_2 and 0·0992 H_2O. C = 69·3; H = 5·4.
II. 0·1620 „ 0·4143 CO_2 „ 0·0790 H_2O. C = 69·6; H = 5·5.
$C_{19}H_{18}O_5$ requires C = 69·6; H = 5·5 per cent.

The determination of the methoxy-groups by Zeisel's method gave the following results:

0·3462 gave 0·7712 AgI. OMe = 28·2.
0·2936 ,, 0·6219 AgI. OMe = 28·0.

$C_{19}H_{18}O_5$, containing three OMe groups, requires OMe = 28·5 per cent.

Trimethylbrazilein melts at 177—178° to a red liquid, and is readily soluble in methyl or ethyl alcohol, chloroform, benzene, acetic acid, or ethyl acetate, but sparingly so in ether or light petroleum, and the solutions stain the skin a deep yellow.

The finely-divided substance dissolves appreciably in boiling water, and the deep yellow solution deposits, on cooling, a voluminous mass of bright yellow needles. The most suitable solvents for crystallising large quantities seem to be ethyl alcohol or ethyl acetate. Trimethylbrazilein crystallises in glistening, yellow plates or in needles, or in hard, amber prisms, often of considerable size, but the conditions under which these different forms are deposited are not known. On one occasion, however, it was observed that a mass of needles which had separated from an alcoholic solution changed in the course of a few hours and while still in the mother liquor into the hard prisms. That trimethylbrazilein, like trimethylbrazilone, crystallises in different modifications is also indicated by an observation, which has twice been made, that, whilst in nearly all cases it melts at 177°, under certain conditions crystals are deposited which melt at 159°, and a substance of this melting point was used in analysis II. In order to determine whether trimethylbrazilein yields an acetyl derivative (compare Herzig, *Monatsh.*, 1898, **19**, 742), the pure substance (2 grams) was digested with acetic anhydride (10 grams) and anhydrous sodium acetate (2 grams), when a dark brown solution was obtained, which deposited the unchanged substance on dilution with water. Trimethylbrazilein is very readily oxidised by nitric or chromic acids, but, on the other hand, it is not very readily attacked by alkaline permanganate in the cold; on warming, oxidation takes place readily, with the formation of large quantities of oxalic acid.

The following description of the crystalline form of trimethylbrazilein was supplied by Mr. George Jerusalem. The crystals are large, amber-coloured prisms, which fracture conchoidally and show no definite cleavage; they belong to the monosymmetric system, and exhibit the two forms *p*{110} and *q*{011} about equally well developed. The form *b*{010} is always present, but is so poorly developed that no measurements were obtained for it.

Crystal System.—Monosymmetric and Pseudorhombic:

$$a:b:c = 0{\cdot}3711 : 1 : 0{\cdot}5860. \quad \beta = 90°6'20''.$$

Forms observed.—*p*{110}, *q*{011}, and *b*{010}.

The following angular measurements were obtained:

Angle.	Number of observations.	Limits.	Mean.	Calculated.
$110 : 1\bar{1}0$	12	40°26′— 40°56′	40°43′30″	—
$110 : \bar{1}10$	11	138 50 —139 39	139 16 0	139°16′30″
$011 : 0\bar{1}1$	7	60 25 — 60 53	60 44 30	—
$\bar{1}10 : 011$	3	80 7 — 80 17	80 10 30	79 57 20
$011 : \bar{1}\bar{1}0$	3	100 8 —100 20	100 13 15	100 13 0
$110 : 011$	6	79 31 — 79 57	79 46 50	—

The crystals were not sufficiently transparent for the satisfactory determinations of the optical properties, but the extinctions on the faces of $p\{110\}$ and $q\{011\}$ were observed to be in accordance with the geometrical symmetry.

Trimethylbrazilein-hydroxylamine, $C_{19}H_{18}O_5,NH_2{\cdot}OH$.*

This substance was obtained as the result of an experiment made with the object of preparing an oxime of trimethylbrazilein.

Hydroxylamine hydrochloride (7 grams) was dissolved in the smallest possible quantity of hot water, mixed with sodium methoxide ($Na = 2{\cdot}3$ grams), and, after filtering from the precipitated sodium chloride, finely-powdered trimethylbrazilein (3 grams) was added to the filtrate.

At first a deep orange solution was produced, but this soon became lighter, and ultimately only very pale yellow. After remaining for several hours, the solution was left to concentrate over sulphuric acid, filtered from a trace of salt, and the concentration continued, when large, colourless prisms separated which were quite free from inorganic matter:

0·1606 gave 0·3755 CO_2 and 0·0853 H_2O. C = 63·8; H = 5·9.
0·1841 „ 0·4334 CO_2 „ 0·0993 H_2O. C = 64·2; H = 6·0.
0·3012 „ 9·5 c.c. nitrogen at 15° and 769 mm. N = 3·8.
0·3107 „ 9·6 c.c. „ „ 19° „ 773 mm. N = 3·6.
$C_{19}H_{21}O_6N$ requires C = 63·5; H = 5·8; N = 3·9 per cent.

Trimethylbrazilein-hydroxylamine is sparingly soluble in water or alcohol, and decomposes at about 150° with evolution of gas. When boiled with acetic acid, sodium carbonate, or ammonia, it is decomposed with separation of trimethylbrazilein.

Salts of Trimethylbrazilein.—One of the most characteristic properties of this substance is the ease with which it combines with concentrated acids to yield deep crimson salts. When a solution of trimethylbrazilein in acetic acid is mixed with concentrated sulphuric acid, an intense crimson solution is formed, which soon deposits a voluminous mass of deep crimson needles of the sulphate.

---

* The addition of hydroxylamine occurs obviously at the quinonoid linking, the process being similar to that which takes place in the formation of trimethyldihydrobrazileinol (p. 1136).

Similarly, the hydrochloride separates in red needles with a violet reflex when concentrated hydrochloric acid is added to the solution of trimethylbrazilein in acetic acid. Both of these salts are decomposed by water with separation of a yellow, crystalline precipitate, which doubtless consists of trimethylbrazilein.

Perhaps the most characteristic salt is the *formate*, $C_{19}H_{18}O_5,CH_2O_2$, which was prepared in large quantities and employed in the purification of crude trimethylbrazilein (p. 1133). When trimethylbrazilein is dissolved in warm formic acid (sp. gr. 1·022), an intense crimson solution is produced, and, if this is mixed with a little water and allowed to remain for a few days, the formate gradually separates in magnificent ruby prisms, which are sometimes of considerable size and possess a quite remarkably brilliant lustre:

0·1516 gave 0·3592 CO_2 and 0·0752 H_2O. C = 64·6; H = 5·5.
0·1511 „ 0·3571 CO_2 „ 0·0744 H_2O. C = 64·4; H = 5·4.
$C_{20}H_{20}O_7$ requires C = 64·5; H = 5·3 per cent.

Trimethylbrazilein formate may be crystallised from small quantities of alcohol, but it is decomposed by much boiling alcohol, yielding a deep yellow solution from which pure trimethylbrazilein separates, usually in needles. The salt is also readily decomposed by water or dilute sodium carbonate.

It is remarkable that, whilst the solution of trimethylbrazilein in formic acid is an intense crimson colour, the corresponding solution in acetic acid is only orange. Attempts to prepare the acetate have been unsuccessful, and it therefore seems possible that trimethylbrazilein does not combine with acetic acid to form a salt corresponding with the formate.

Action of Potassium Hydroxide on Trimethylbrazilein. Formation of Trimethyldihydrobrazileinol, $C_{16}H_{10}O_2(OMe)_3 \cdot OH$.

Trimethylbrazilein is insoluble in dilute potassium hydroxide, but, if the finely-divided substance (in quantities of not more than 5 grams) is boiled with water (150 c.c.) and then concentrated potassium hydroxide (5 grams) added in small quantities at a time, it gradually dissolves to a pale brown solution. This is filtered from traces of unchanged trimethylbrazilein, and the filtrate run in a thin stream into an excess of dilute acetic acid kept cooled by ice and well stirred by a turbine. The drab precipitate which separates is collected, left in contact with porous porcelain until quite dry, and then rubbed in a mortar with cold alcohol, which dissolves much dark-coloured resinous matter. The mass is transferred to the filter, the precipitate well washed with small quantities of alcohol until the filtrate is only pale yellow, and then crystallised from much boiling alcohol, from which *trimethyldihydrobrazileinol* separates in glistening, yellow prisms. The dark-coloured mother liquors are digested for some hours with animal charcoal, filtered, and then allowed to concentrate spontaneously in the air, and the dark crusts which gradually separate are then purified by recrystallisation from alcohol :

0·1489 gave 0·3592 CO_2 and 0·0780 H_2O. C = 65·9 ; H = 5·9.
0·1467 „ 0·3572 CO_2 „ 0·0801 H_2O. C = 66·4 ; H = 5·8.
$C_{19}H_{20}O_6$ requires C = 66·3 ; H = 5·8 per cent.

The determination of the methoxy-groups by Zeisel's method gave the following results :

0·3491 gave 0·6979 AgI. OMe = 26·4.
$C_{19}H_{20}O_6$, containing three OMe groups, requires OMe = 27·0 per cent.

When heated in a capillary tube, trimethyldihydrobrazileinol gradually darkens in colour, finally becomes deep red, and melts at about 177°, the melting point of trimethylbrazilein, into which it is obviously converted during the process (p. 1138). It is readily soluble in boiling chloroform or ethyl acetate, and moderately so in methyl and ethyl alcohols, but, with the exception of the first named, it dissolves sparingly in these solvents in the cold. It is also sparingly soluble in benzene, and almost insoluble in light petroleum. It separates from its solutions in well-defined, four-sided prisms, and, when quite pure, has only a pale yellow colour.

Trimethyldihydrobrazileinol is not readily attacked by concentrated potassium hydroxide even on boiling, and attempts to prepare decomposition products by digesting with methyl- or ethyl-alcoholic potash were unsuccessful, since the substance was either recovered unchanged or yielded resinous products from which nothing crystalline could be obtained. When its solution in potassium hydroxide is mixed with hydroxylamine hydrochloride, the brown colour rapidly becomes paler, and, after several hours, a colourless solution is obtained from which acetic acid deposits a colourless precipitate, which, however, rapidly becomes yellow in contact with air. If hydrogen peroxide (30 per cent.) is added to a solution of trimethyldihydrobrazileinol in excess of potassium hydroxide, a perfectly colourless precipitate is rapidly deposited, which crystallises from alcohol in almost colourless, four-sided prisms :

0·1679 gave 0·4087 CO_2 and 0·0896 H_2O. C = 66·4 ; H = 5·9.
$C_{19}H_{20}O_6$ requires C = 66·3 ; H = 5·8 per cent.

This substance melted when rapidly heated at about 185°, is readily soluble in dilute potassium hydroxide, and evidently consists of trimethyldihydrobrazileinol, which, therefore, when quite pure is almost colourless.

What was difficult to understand, at first, is that hydrogen peroxide should precipitate this substance from a strongly alkaline solution. Experiment showed, however, that other phenols behave in a similar manner, since, for example, a solution of resorcinol methyl ether, $C_6H_4(OMe)\cdot OH$, in excess of dilute potassium hydroxide is also precipitated by hydrogen peroxide. Possibly the hydrogen peroxide converts the potassium hydroxide into peroxide, which is no longer able to dissolve the phenolic substances.

Conversion of Trimethyldihydrobrazileinol into Trimethylbrazilein.

In describing its behaviour in a capillary tube, it has already been pointed out that trimethyldihydrobrazileinol is evidently converted into trimethylbrazilein by the action of heat, and this interesting change takes place, apparently almost quantitatively, under the following conditions. The finely-divided substance is digested with ten times its weight of glacial acetic acid for two minutes and the deep orange solution poured into water, when the milky liquid soon deposits a crystalline precipitate, which, after washing with water and dilute potassium hydroxide, crystallises from alcohol in deep yellow prisms:

0·1356 gave 0·3449 CO_2 and 0·0698 H_2O. C = 69·4; H = 5·7.

$C_{19}H_{18}O_5$ requires C = 69·6; H = 5·5 per cent.

This substance melted at 177° and consisted, as direct comparison proved, of pure trimethylbrazilein.

Tetramethyldihydrobrazileinol, $C_{16}H_{10}O_2(OMe)_4$.

It has been shown on p. 1133 that one of the principal products of the methylation of trimethylbrazilein with potassium hydroxide and methyl sulphate is a substance which is separated from trimethylbrazilein by treatment with ether in the cold and obtained from the ethereal solution as an ochreous mass. In order to remove traces of trimethylbrazilein which this product undoubtedly contained, it (100 grams) was dissolved in a little alcohol and digested with alcoholic potash (KOH = 15 grams) for fifteen minutes at the boiling point.

The solution was run in a thin stream into much water, kept vigorously agitated by a turbine, and allowed to remain overnight, and the pale ochreous precipitate was then collected, well washed with water, and left in contact with porous porcelain and over sulphuric acid in a vacuum desiccator until quite dry. The examination of this substance showed that it consisted essentially of tetramethyldihydrobrazileinol (compare the analogous formation of pentamethyldihydrohæmateinol, p. 1143), but it was still very impure, since a determination of the methoxy-groups yielded MeO = 27·5, whereas the formula $C_{16}H_{10}O_2(OMe)_4$ requires MeO = 34·3 per cent.

The properties of this substance render it very difficult to purify, since it is excessively soluble in nearly all organic solvents and exhibits very little tendency to crystallise. In light petroleum (b. p. 60—70°), it is, however, sparingly soluble, and if the crude product (10 grams) is digested with light petroleum (500 c.c.) most of it dissolves, leaving a dark brown resin. The solution was decanted, digested with animal charcoal, concentrated to about 100 c.c. (under 200 mm. pressure), poured into a beaker, and allowed to stand for some days, when hard, apparently amorphous crusts formed on the bottom and sides of the beaker. The analytical results obtained were now much more satisfactory, and indicated that this substance consisted of nearly pure tetramethyldihydrobrazileinol:

0·1471 gave 0·3558 CO_2 and 0·081 H_2O. C = 66·0; H = 6·1.

$C_{20}H_{22}O_6$ requires C = 67·0; H = 6·1 per cent.

The determination of the methoxy-groups by Zeisel's method gave:

0·2107 gave 0·529 AgI. MeO = 33·2

$C_{20}H_{22}O_6$, containing four MeO groups, requires MeO = 34·3 per cent.

The unsatisfactory nature of this substance, especially when compared with pentamethylhæmateinol (p. 1143), which crystallises with such facility, made it appear probable that its inability to crystallise properly was due to the impurity which it still contained, and, in order to test this point, it was decided to prepare the substance from trimethyldihydrobrazileinol by direct methylation.

Trimethyldihydrobrazileinol (4 grams) was dissolved in methyl alcohol, and mixed with methyl-alcoholic potash (KOH = 5 grams) and methyl sulphate (4 grams), the whole being well cooled during the addition.

A further quantity of methyl-alcoholic potash (KOH = 2 grams) and methyl sulphate (4 grams) was then added, and, after remaining overnight, the whole was diluted with water, when a yellow, amorphous precipitate separated. This was collected, washed well, and allowed to remain over sulphuric acid in a vacuum desiccator until quite dry, but the pale ochreous mass still showed the same inability to crystallise which had been observed in the case of the previous specimen. It separated from light petroleum in crusts which could scarcely be called crystalline, but the analytical results were now more satisfactory:

0·1333 gave 0·3242 CO_2 and 0·0763 H_2O. C = 66·4; H = 6·3.
0·1466 „ 0·3580 CO_2 „ 0·0832 H_2O. C = 66·6; H = 6·1.
$C_{20}H_{22}O_6$ requires C = 67·0; H = 6·1 per cent.

The methoxy-determination gave the following results:

0·147 gave 0·3558 AgI. MeO = 33·2.
0·1595 „ 0·3938 AgI. MeO = 33·6.
$C_{16}H_{10}O_2(OMe)_4$ required MeO = 34·3 per cent.

Tetramethyldihydrobrazileinol softens at 55° and becomes transparent at about 60°, but it has no definite melting point.

It is very readily soluble in methyl or ethyl alcohol, chloroform, benzene, or ether, and is also appreciably, although sparingly, so in boiling water. It is almost insoluble in cold light petroleum. It dissolves in formic acid with an intense eosin-red colour, and is reprecipitated by much water.

The Methylation of Haematein.

In preparing the large quantities of hæmatein required for these experiments, the following method, based on the observations of J. J. Hummel and A. G. Perkin (Trans., 1882, **41**, 368), was employed.

Finely-powdered *pure* hæmatoxylin (15 grams) is dissolved in water (150 c.c.) and concentrated ammonia (15 c.c.), and a rapid current of air drawn through the solution for about six hours, all rise of temperature being avoided by cooling in running water during the operation. Dilute acetic acid (about 250 c.c. of 10 per cent.) is heated on the water-bath, and the product of oxidation added in a thin stream, steam being passed during the addition, when hæmatein separates in crystals with the characteristic silver lustre. The product is filtered, washed with water and then with methyl alcohol, and drained on porous porcelain.

The yield of hæmatein varies considerably in different experiments, it is sometimes 80 per cent. and sometimes as low as 50 per cent. of the theoretical. The methylation of hæmatein is a very difficult operation, much more so than the methylation of brazilein, and this is due partly to the readiness with which hæmatein is oxidised in alkaline solution and partly to the solubility of the product of methylation. The operation is carried out in a large, round-bottomed flask provided with a cork and tubes, so that oxidation may be avoided as far as possible by passing coal gas.

Hæmatein (80 grams) is mixed in the flask with water (400 c.c.) ice

(200 grams), and potassium hydroxide (217 c.c. of 43 per cent.), and well shaken until the hæmatein has completely dissolved. Methyl sulphate (230 c.c.) is added in one portion, the flask well agitated, carefully cooled in running water, and a current of coal gas passed during the whole operation. After about three-quarters of an hour, a further quantity of potassium hydroxide (150 c.c.) is added in several small quantities, and the shaking continued for fifteen minutes; the flask in then allowed to remain for three to four hours in running water. The precipitate * is collected on cloth on a filter frame, well washed, and drained on porous porcelain; it is then treated as explained in the next section.

The dark red filtrate is acidified with acetic acid, saturated with salt, and the precipitate collected, washed with water, and further methylated by dissolving in water (300 c.c.) and potassium hydroxide (72 c.c. of 43 per cent.) and shaking with methyl sulphate (86 c.c.), the precipitate which forms being again collected and drained on porous porcelain as before. This process is repeated with the mother liquor until no more precipitate forms, but, even under the most favourable conditions, the yield of the crude product of methylation, insoluble in alkalis, is very unsatisfactory and is seldom more than 40 per cent of the hæmatein employed.

Tetramethylhaematein, $C_{16}H_8O_2(OMe)_4$, *Tetramethyldihydrohaemateinol*, $C_{16}H_9O_2(OMe)_4{\cdot}OH$, *and Pentamethyldihydrohaemateinol*, $C_{16}H_9O_2(OMe)_5$.

The crude product of the methylation of hæmatein, obtained as explained in the last section and which is insoluble in cold dilute potassium hydroxide, contains *tetramethylhaematein* and *pentamethyldihydrohaemateinol*,† and these may be separated by taking advantage of the fact that the pentamethyl compound is more soluble in cold ethyl acetate (or in boiling light petroleum) than the tetramethyl compound. In the one case, the crude mass is ground up with successive small quantities of cold ethyl acetate, until the dark resinous impurity and much of the pentamethyl compound has been removed, and the residual ochreous mixture of the tetra- and penta-methyl compounds is separated into its constituents by fractional crystallisation from ethyl acetate, when the tetramethyl compound separates first. The ethyl acetate mother liquors are digested with animal charcoal, filtered, the filtrate allowed to concentrate spontaneously in the air, and the dark crystalline crusts which separate are then purified as before by crystallisation from ethyl acetate or, better, from alcohol. When much resinous matter is present, separation by means of light petroleum has frequently been found advantageous. The crude mass is repeatedly extracted on the water-bath with much light petroleum (b. p. 100—110°), which dissolves the pentamethyl compound the more readily, and from which ochreous crusts are deposited on cooling.

---

* It sometimes happens that no precipitate separates, in which case a further quantity of methyl sulphate (86 c.c.) and potassium hydroxide (56 c.c.) is added and the shaking continued as before.

† Generally speaking, the latter is present in much the larger quantity, and in one large preparation the product consisted entirely of crude pentamethyldihydrohæmateinol.

After collecting, the filtrate is used to again extract the undissolved mass, the process being repeated several times until an insoluble, black resin remains. Tetramethylhæmatein and pentamethyldihydrohæmateinol are then separated from the crude crystalline mass as before by fractional crystallisation from ethyl acetate.

Tetramethylhaematein.—This substance is obtained pure by repeated crystallisation from alcohol or ethyl acetate, from either of which it separates in beautiful amber-coloured, rhombic prisms with truncated ends. For analysis, it was dried over sulphuric acid.

0·1578 gave 0·3878 CO_2 and 0·0823 H_2O. C = 67·0; H = 5·8.
0·1738 „ 0·4279 CO_2 „ 0·0891 H_2O. C = 67·1; H = 5·7.
$C_{20}H_{20}O_6$ requires C = 67·4; H = 5·6 per cent.

Tetramethylhaematein melts at 210° to a red oil, which rapidly decomposes and is readily soluble in boiling alcohol or ethyl acetate, but sparingly so in these solvents in the cold. It is also sparingly soluble in benzene and almost insoluble in light petroleum. It dissolves in formic acid with an intense crimson colour, but the formate does not, like trimethylbrazilein formate (p. 1136), appear to crystallise readily; it is also very readily soluble in acetic acid, yielding a deep orange-brown solution.

Tetramethylhæmatein dissolves in concentrated sulphuric acid in the cold with an intense crimson colour, but this soon begins to change, and if warmed at 60° the change to orange is very rapid.

The solution acquires a faint green fluorescence, which is not nearly so marked as that exhibited by trimethylbrazilein under the same conditions. When the orange solution is poured into water, a bright red, gelatinous precipitate separates, which is described on p. 1151.

Tetramethyldihydrohaemateinol.—When tetramethylhæmatein is ground to a paste with water and warmed with dilute potassium hydroxide, it rapidly dissolves to a pale claret solution. This was filtered into an excess of cold dilute acetic acid, and the pale ochreous very voluminous precipitate was collected, washed with water, dried on porous porcelain, and crystallised from alcohol:

0·1477 gave 0·3482 CO_2 and 0·0800 H_2O. C = 64·3 ; H = 6·1.
0·1342 „ 0·3153 CO_2 „ 0·0718 H_2O. C = 64·2 ; H = 6·0.
$C_{20}H_{22}O_7$ requires C = 64·2 ; H = 5·9 per cent.

Tetramethyldihydrohaemateinol melts at 183°, and is readily soluble in boiling alcohol, ethyl acetate, or chloroform, but sparingly so in the two first mentioned in the cold as also in benzene, and it is almost insoluble in light petroleum.

It dissolves readily in glacial acetic acid, and the solution, on boiling, becomes a deep red, elimination of water and formation of tetramethylhæmatein taking place apparently during this operation (compare the analogous formation of trimethylbrazilein from trimethyldihydrobrazileinol, p. 1138).

Pentamethyldihydrohaemateinol.—The separation of this substance from the crude product of the methylation of hæmatein is described above. After repeated recrystallisation from alcohol and then from ethyl acetate, the following results were obtained on analysis:

0·1378 gave 0·3284 CO_2 and 0·0791 H_2O. C = 65·0 ; H = 6·3.
0·1470 „ 0·3502 CO_2 „ 0·0866 H_2O. C = 65·0 ; H = 6·4.
$C_{21}H_{24}O_7$ requires C = 65·0 ; H = 6·2 per cent.

The methoxy-groups were determined with the following result:

0·2691 gave 0·7770 AgI. MeO = 38·2.
$C_{21}H_{24}O_7$, containing five MeO groups, requires MeO = 39·8 per cent.

Pentamethyldihydrohaemateinol melts at 159—160°, and is readily soluble in boiling alcohol, ethyl acetate, or chloroform, but sparingly so in light petroleum. It separates from alcohol in very pale yellow, four-sided plates, but, when its solution in ethyl acetate is allowed to concentrate spontaneously, it is frequently deposited in well-defined, six-sided plates or prisms. It is curious that this compound should crystallise with such facility, whereas the corresponding tetramethyldihydrobrazileinol (p. 1139) is so difficult to obtain in a crystalline condition.

Pentamethyldihydrohæmateinol dissolves in concentrated sulphuric acid with a brilliant crimson colour, which changes only slowly at the ordinary temperature. If the solution is warmed at 60°, however, it rapidly becomes pale reddish-brown, and acquires a very faint green fluorescence which is not nearly so marked as in the case of tetramethyldihydrobrazileinol. When poured into water, a crimson salt separates, which dissolves readily in hot water and, on slowly cooling, crystallises beautifully in bunches of orange-red needles (see p. 1152).

Oxidation of Tetramethyldihydrobrazileinol with Chromic Acid.

Formation of Trimethylbrazilone and other Products.

In carrying out this oxidation, tetramethyldihydrobrazileinol (12 grams) was dissolved in glacial acetic acid (60 c.c.) in a large beaker fitted with a mechanical stirrer, and then chromic acid (12 grams) dissolved in water (20 c.c.) was gradually added, the whole being carefully cooled by running water during the operation. The product was poured in a thin stream into much water, saturated with salt, and allowed to stand overnight; the precipitate which had separated was collected and purified by many crystallisations from ethyl acetate, alcohol, and finally from methyl ethyl ketone:

0·1886 gave 0·4596 CO_2 and 0·0882 H_2O. C = 66·4; H = 5·2.
$C_{19}H_{18}O_6$ requires C = 66·6; H = 5·3 per cent.

The determination of the methoxy-groups gave the following result:

0·3202 gave 0·6439 AgI. MeO = 26·6.
$C_{19}H_{18}O_6$, containing three MeO groups, requires MeO = 27·2 per cent.

That this substance, which separated from methyl ethyl ketone in colourless prisms and melted at 160°, is trimethylbrazilone (Trans., 1902, **81**, 1041) was proved by conversion into α-acetylanhydrotrimethylbrazilone by boiling with acetic anhydride and sodium acetate.

After crystallising from acetic acid, this derivative melted at 175°, and the melting point was unchanged when it was mixed with a specimen of the acetyl compound which had been obtained on a previous occasion (*loc. cit.*, p. 1045). An analysis was also carried out:

0·1246 gave 0·3128 CO_2 and 0·0552 H_2O. C = 68·5; H = 4·9.
$C_{21}H_{18}O_6$ requires C = 68·8; H = 4·9 per cent.

Trimethylbrazilone is dimorphous, and its melting point varies in a remarkable manner according to the solvent from which it is crystallised. Gilbody and Perkin (*loc. cit.*, p. 1041) state that, when crystallised from alcohol, it melts at about 185°, and that subsequent repeated crystallisation from benzene causes the melting point to sink to 167°. Herzig (*Monatsh.*, 1902, **23**, 172) gives 160° as the melting point after crystallisation from acetic acid, and we have now observed that this substance also melts at 160° when it is repeatedly recrystallised from methyl ethyl ketone. When the trimethylbrazilone, previously obtained from trimethylbrazilin by oxidation, was crystallised in this way and mixed with the specimen obtained from tetramethyldihydrobrazileinol, the mixture melted at 160°.

The mother liquors from the purification of the trimethylbrazilone obtained in the above oxidation were carefully examined, and found to contain two neutral substances melting at 98° and 142—144° respectively.

These were present only in very small quantity, and we have no clue to their nature, but sufficient of the former was obtained for the following analysis:

0·0945 gave 0·2012 CO_2 and 0·0415 H_2O. C = 58·1; H = 4·9.

$C_{19}H_{18}O_9$ requires C = 58·5; H = 4·6 per cent.

The filtrate from the crude trimethylbrazilone, containing common salt, was extracted twenty times with ether on the machine, the ether evaporated, and the dark residual liquid distilled from the water-bath under 20 mm. pressure in order to remove as much acetic acid as possible. After standing for twenty-four hours in the ice-chest, a considerable quantity of a dark solid had separated, which was collected and the filtrate again heated under 20 mm. on the water-bath, and this operation repeated until no further separation of solid took place even when the thick syrup remained in the ice-chest for several days. The solid was boiled with much water, the solution filtered from resinous matter, decolorised as far as possible with animal charcoal, and evaporated to a small bulk, when an ochreous substance separated, which, after several crystallisations from water, softened at about 195° and melted at 210°:

0·1417 gave 0·3050 CO_2 and 0·0735 H_2O. C = 58·7; H = 5·7.
0·1322 „ 0·2808 CO_2 „ 0·0661 H_2O. C = 57·9; H = 5·6.

$C_{13}H_{16}O_6$ requires C = 58·2; H = 5·9 per cent.

This curious substance has the properties of a lactone. When mixed with cold dilute sodium carbonate, it becomes pink and only slowly dissolves, but, on warming, a deep claret solution is at once obtained, and potassium hydroxide dissolves it with the same colour.

It dissolves also readily in hot barium hydroxide with a claret colour, which on boiling becomes light brown, and on acidifying an ochreous, crystalline substance separates, which crystallises from water, melts at about 163°, and is probably not the hydroxy-acid corresponding with the lactone, because the solution in sodium carbonate is colourless. That this substance of melting point 210° is derived from the catechol nucleus of brazilin was proved by fusion with potassium hydroxide, when, on acidifying and extracting with ether, a syrup was obtained which yielded an intense catechol reaction with ferric chloride.

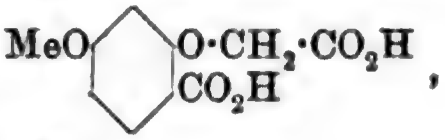
The aqueous mother liquors from the purification of the above substance yielded, on concentration and careful fractional crystallisation, a second substance, which, under the microscope, was seen to consist of a mass of separate threads and to be quite homogeneous. This substance melted at about 190°, and yielded on analysis:

0·1369 gave 0·2716 CO_2 and 0·0761 H_2O. C = 54·1; H = 6·2.

$C_{13}H_{18}O_7$ requires C = 54·5; H = 6·3 per cent.

It contains therefore one molecule of water more than the substance of melting point 210°, to which it is obviously closely related, since it also is only slowly dissolved by sodium carbonate in the cold, but dissolves readily, with a deep claret colour, on warming; it also gives the catechol reaction when fused with potassium hydroxide.

In a second series of experiments on the oxidation of tetramethyldihydrobrazileinol with chromic acid, the same substances were again obtained in small quantities, and, in addition, two others were isolated, namely, an acid which melted at 174° and a neutral substance which melted at 170°; of these, the former was sparingly, and the latter readily, soluble in water. The *acid* of melting point 174° is *2-carboxy-5-methoxyphenoxyacetic acid*,



since it yielded on analysis:

0·1176 gave 0·2288 CO_2 and 0·0482 H_2O. C = 53·0; H = 4·5.

$C_{10}H_{10}O_6$ requires C = 53·0; H = 4·5 per cent,

and when mixed with a specimen of this acid which had been previously prepared (Trans., 1901, **79**, 1407) there was no alteration in melting point.

The neutral *substance* shrinks at 163° and melts at about 170°; it is very readily soluble in water, alcohol, or ethyl acetate, but sparingly so in benzene or ether, and separates, when its solution in much ether is concentrated, as a voluminous mass of colourless needles.

Dried at 100°, it yielded the following analytical results:

0·1375 gave 0·3050 CO_2 and 0·0790 H_2O. C = 60·5; H = 6·4.

0·1157 ,, 0·2606 CO_2 ,, 0·0647 H_2O. C = 61·4; H = 6·2.

$C_{13}H_{16}O_5$ requires C = 61·9; H = 6·3 per cent.

When the substance was crystallised from water, it separated in needles, and contained H_2O more than the substance which had been dried at 100°:

0·1290 gave 0·2760 CO_2 and 0·0762 H_2O. C = 58·3; H = 6·6.

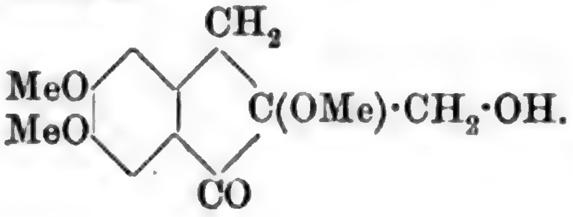
$C_{13}H_{18}O_6$ requires C = 57·8; H = 6·6 per cent.

The methoxy-determination gave the following result:

0·175 gave 0·4622 AgI. MeO = 34·8.

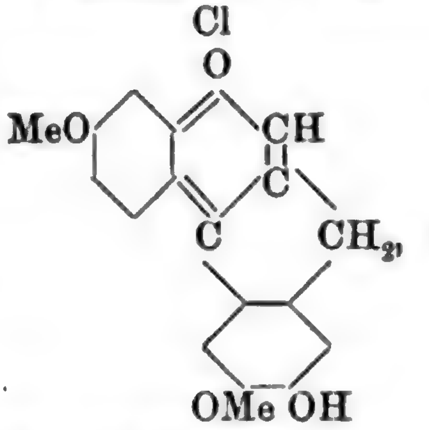
$C_{13}H_{18}O_6$, containing three MeO groups, requires MeO = 34·4 per cent.

The solution of this substance in water is slightly acid to litmus, but the addition of a drop of $N/10$-potassium hydroxide makes it alkaline to phenolphthalein. That the substance is derived from the catechol nucleus of brazilin was shown by the fact that, after fusing with potassium hydroxide, acidifying, and extracting with ether, an intense catechol reaction was obtained on the addition of ferric chloride. It is possible that this substance may have the constitution represented by the formula



The Pyranol Salts Derived from Trimethylbrazilein.

5'-Hydroxy-4' : 7-dimethoxy-4 : 3-indenobenzopyranol (1 : 4) *Anhydro-hydrochloride*, $2H_2O$, *the Anhydro-hydrogen Sulphate, and Other Derivatives.*



Trimethylbrazilein dissolves in glacial acetic acid with an orange-red colour, and, if concentrated sulphuric acid is added, a deep crimson solution is formed, which gradually fades, acquires a green fluorescence, and deposits a splendid crimson anhydro-hydrogen sulphate on dilution with water. Another way of preparing the anhydro-hydrogen sulphate is to dissolve trimethylbrazilein (1 gram) in sulphuric acid (10 c.c.) and to warm the deep orange-red solution at 50°, when it soon becomes pale brown and exhibits a striking fluorescence. On diluting with water, the anhydro-hydrogen sulphate separates as a brilliant crimson precipitate, which was collected, washed with dilute sulphuric acid, and crystallised from glacial acetic acid, from which it separated in orange-red needles or four-sided plates with a green, metallic lustre :

0·2026 gave 0·4085 CO_2 and 0·0815 H_2O. C = 55·0 ; H = 4·4.
0·1764 ,, 0·4840 CO_2 ,, 0·0630 H_2O. C = 54·8 ; H = 4·0.
0·4422 ,, 0·2678 $BaSO_4$. SO_4 = 24·9.
$C_{18}H_{15}O_4,HSO_4$ requires C = 55·1 ; H = 3·8 ; SO_4 = 24·5 per cent.

This *anhydro-hydrogen sulphate* is decomposed by boiling with water with separation of a black resin; the addition of potassium hydroxide to its aqueous solution caused the precipitation of a brown, amorphous substance, which is soluble in excess of alkali, and is probably the free pyranol base.

The *anhydrohydrochloride* is prepared by dissolving the anhydrohydrogen sulphate in much hot dilute hydrochloric acid and rapidly filtering and cooling the solution, when a voluminous mass of brick-red needles separates. The salt was collected, washed with dilute hydrochloric acid, and dried over sulphuric acid and potassium hydroxide in a vacuum:

0·1720 gave 0·3705 CO_2 and 0·0783 H_2O. C = 58·7; H = 5·0.
0·3178 „ 0·1349 AgCl. Cl = 10·5.
$C_{18}H_{15}O_4Cl,2H_2O$ requires C = 58·8; H = 5·1; Cl = 9·7 per cent.

This *anhydrohydrochloride* is readily decomposed when it is boiled with water.

The *platinichloride* is obtained as a brick-red precipitate when platinic chloride is added to a warm solution of the anhydrohydrochloride in excess of hydrochloric acid. It was collected, washed with dilute hydrochloric acid, and dried over sulphuric acid:

0·5366 gave 0·1015 Pt. Pt = 18·9.
$(C_{18}H_{15}O_4Cl)_2PtCl_4,2H_2O$ requires Pt = 18·8 per cent.

The *anhydroferrichloride*.—In order to prepare this double salt, ferric chloride is added to a hot solution of the hydrochloride in excess of hydrochloric acid, and the yellowish-brown precipitate collected. The substance is sparingly soluble in acetic acid, and separates as a beautiful green, metallic mass consisting of minute leaflets. For analysis, it was dried at 100°:

0·1220 gave 0·1964 CO_2 and 0·0347 H_2O. C = 43·9; H = 3·2.
$_{18}H_{15}O_4,FeCl_4$ requires C = 43·8; H = 3·2 per cent.

This salt darkens at 225°, and gradually decomposes as the temperature rises, but it does not melt even at 240°.

The *anhydrohydrobromide*.—This beautiful substance is readily obtained by warming the anhydro-hydrogen sulphate with aqueous-alcoholic hydrobromic acid. The filtered solution is allowed to cool, when the salt separates as a mass of microscopic needles with a splendid beetle-green lustre:

0·1102 gave 0·2247 CO_2 and 0·0451 H_2O. C = 55·6; H = 4·5.
$C_{18}H_{15}O_4Br,H_2O$ requires C = 55·0; H = 4·3 per cent.

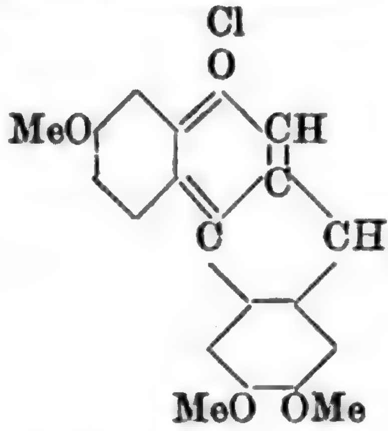
The *anhydro-cadmium bromide* is prepared by adding cadmium bromide to a solution of the anhydrohydrobromide in alcohol containing a little hydrobromic acid. The light brown precipitate, which separates at once, is collected, washed with water, and dried over sulphuric acid in a vacuum :

0·1216 gave 0·1043 AgBr. Br = 36·5.

$C_{18}H_{15}O_4,CdBr_3$ requires Br = 37·1 per cent.

The Pyranol Salts Derived from Tetramethyldihydrobrazileinol.

7 : 4 : 5'-*Trimethoxy*-4 : 3-*indenobenzopyranol* (1 : 4) *Anhydrohydrochloride*, and *Other Salts.*



Tetramethyldihydrobrazileinol dissolves in concentrated sulphuric acid with a deep orange-red colour, but this soon becomes paler and the solution acquires an intense uranium-green fluorescence.

After remaining for an hour at the ordinary temperature, the solution was poured on powdered ice, when a splendid orange-red precipitate separated, which was, at first, rather gelatinous, but became more crystalline on standing. It was collected, washed with a little dilute sulphuric acid, in which it is rather sparingly soluble, and drained on porous porcelain.

When this red anhydro-hydrogen sulphate is stirred with glacial acetic acid, the colour changes to an ochre-yellow, a change doubtless due to loss of water of crystallisation. After drying over potassium hydroxide, the ochreous substance gave the following results on analysis :

0·2238 gave 0·4490 CO_2 and 0·0899 H_2O. C = 54·3 ; H = 4·5.

0·6236 ,, 0·3564 $BaSO_4$. SO_4 = 22·6.

$C_{19}H_{17}O_4,HSO_4,H_2O$ requires C = 53·8 ; H = 4·3 ; SO_4 = 22·6 per cent.

The red *anhydro-hydrogen sulphate* gave less SO_4, but the analytical results were not sufficiently sharp to show the number of molecules of water of crystallisation which the salt contains. It decomposes when warmed with water with separation of a dark brown, resinous mass, and its aqueous solution yields a yellowish-brown precipitate, insoluble in excess, when it is mixed with dilute potassium hydroxide or ammonia. The anhydro-hydrogen sulphate dissolves in formic acid or acetic acid with a splendid fluorescence, and it may be recrystallised from warm glacial acetic acid containing a trace of sulphuric acid.

The aqueous and methyl-alcoholic solutions also exhibit a striking fluorescence.

The *anhydrohydrochloride*.—The anhydro-hydrogen sulphate dissolves in hot dilute hydrochloric acid, and, on cooling, the hydrochloride separates in beautiful glistening, orange needles, which are sparingly soluble in hydrochloric acid and the aqueous solution of which exhibits a fine green fluorescence. After drying over sulphuric acid and potassium hydroxide, the salt was salmon-coloured:

0·2233 gave 0·4733 CO_2 and 0·115 H_2O. C = 57·8; H = 5·7.
0·3181 ,, 0·1212 AgCl. Cl = 9·4.
$C_{19}H_{17}O_4Cl,3H_2O$ requires C = 57·3; H = 5·7; Cl = 8·9 per cent.

The *platinichloride* separates as a buff, amorphous precipitate when platinic chloride is added to a warm solution of the anhydrohydrochloride in hydrochloric acid:

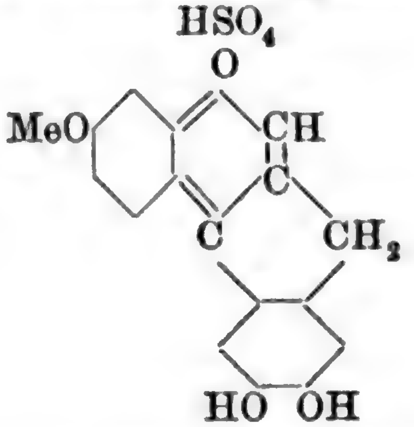
0·3910 gave 0·073 Pt. Pt = 18·6.
$(C_{19}H_{17}O_4Cl)_2PtCl_4,2H_2O$ requires Pt = 18·4 per cent.

The *anhydroferrichloride* is readily prepared by adding concentrated ferric chloride to a solution of the anhydrohydrochloride in aqueous alcoholic hydrochloric acid. The orange precipitate is collected and crystallised from glacial acetic acid, from which it separates in brown leaflets with a striking coppery lustre. For analysis, the substance was dried at 100°:

0·1218 gave 0·1998 CO_2 and 0·037 H_2O. C = 44·9; H = 3·4.
$C_{19}H_{17}O_4,FeCl_4$ requires C = 44·9; H = 3·4 per cent.

The Pyranol Salts Derived from Mono- or Di-methylbrazilein.

4′ : 5′-*Dihydroxy*-7-*methoxy*-4 : 3-*indenobenzopyranol* (1 : 4) *Anhydro-hydrogensulphate*,



, $2H_2O$.

In order to prepare this salt, dimethylbrazilein (probably containing monomethylbrazilein), prepared as described on p. 1132, is dissolved in sulphuric acid. The deep crimson solution is warmed on the water-bath, and, as soon as the colour has completely changed, the fluorescent solution is poured into water, which causes a sparingly soluble orange precipitate to separate. This is collected, crystallised from much acetic acid, and dried on porous porcelain in the air:

0·1174 gave 0·2134 CO_2 and 0·0450 H_2O. C= 9·6; H=4·3.

$C_{17}H_{13}O_4,HSO_4,2H_2O$ requires C=49·3; H=4·3 per cent.

The complex *ferrichloride.*—The anhydro-hydrogen sulphate may be converted into other salts in the usual manner. When it is dissolved in alcoholic hydrochloric acid, a yellow solution is obtained, from which ferric chloride precipitates a yellow substance. It is sparingly soluble in boiling glacial acetic acid, and separates, on cooling, in dark brownish-green crystals, which, after drying on porous porcelain in the air, gave the following results on analysis:

0·1330 gave 0·2440 CO_2 and 0·0421 H_2O. C=50·0; H=3·5.

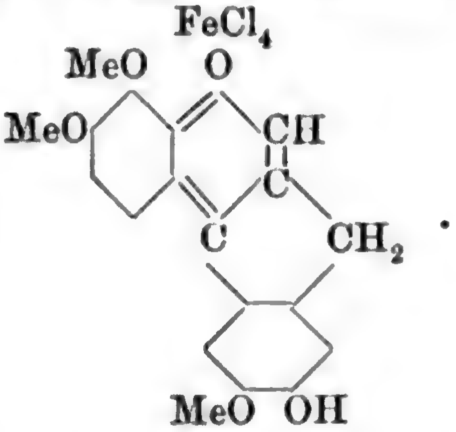
0·2848 „ 0·0203 Fe_2O_3. Fe=7·1.

$C_{17}H_{13}O_4Cl,FeCl_3,C_{17}H_{13}O_4Cl,H_2O$ requires C=50·2; H=3·4; Fe=6·9 per cent.

It appears therefore that this ferrichloride has an abnormal composition.

Pyranol Salts Derived from Tetramethylhaematein.

*5'-Hydroxy-*7:8:4'*-trimethoxy-*4:3*-indenobenzopyranol* (1:4) *Anhydro-ferrichloride,*



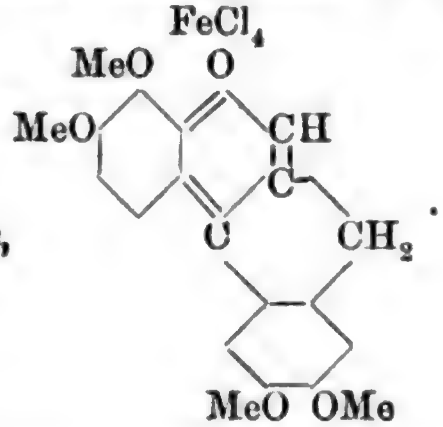
.

Tetramethylhæmatein dissolves in sulphuric acid with a characteristic carmine colour, and, on warming, this changes to yellowish-brown, but the solution does not fluoresce strongly as in the case of trimethylbrazilein (p. 1147). When this solution is poured into water, a gelatinous, orange-red substance is obtained, which is very similar to the red anhydro-hydrogen sulphate produced from trimethylbrazilein under the same conditions. It dissolves in hot alcoholic hydrochloric acid, and, on cooling, the solution deposits a brownish-yellow, gelatinous anhydrohydrochloride. This anhydrohydrochloride yields double salts when treated with metallic chlorides in the usual way, and these are gelatinous when first precipitated. Thus the anhydroferrichloride is obtained as an orange-red, gelatinous precipitate when ferric chloride is added to the solution of the anhydrohydrochloride. It was collected and recrystallised from glacial acetic acid, from which it separated as an orange-brown, crystalline mass, which, under the microscope, was seen to consist of well-defined, elongated prisms. For analysis, the substance was dried at 100°:

0·1308 gave 0·2082 CO_2 and 0·0391 H_2O. C = 43·4 ; H = 3·3.
$C_{19}H_{17}O_5,FeCl_4$ requires C = 43·7 ; H = 3·3 per cent.

Pyranol Salts Derived from Pentamethyldihydrohaemateinol.

7 : 8 : 4′ : 5′-*Tetramethoxy*-4 : 3-*indenobenzopyranol* (1 : 4) *Anhydroferrichloride*,



Pentamethyldihydrohæmateinol dissolves in sulphuric acid, producing a crimson solution, which, when heated on the water-bath, becomes yellow, owing to the formation of the pyranol anhydro-hydrogen sulphate. On pouring into water, an orange salt is precipitated, which is much more soluble than the salt which is obtained from tetramethyldihydrobrazileinol under the same conditions. When dissolved in hot aqueous alcoholic hydrochloric acid, a yellow solution of the anhydrohydrochloride is obtained, from which all the usual double salts may be prepared. The *anhydroferrichloride* is an orange-yellow precipitate, which crystallises from acetic acid in chocolate-coloured needles, and melts at 190°. Dried at 100°, the following results were obtained on analysis:

0·1270 gave 0·2092 CO_2 and 0·0427 H_2O. C = 44·9 ; H = 3·7.
$C_{20}H_{19}O_5,FeCl_4$ requires C = 44·9 ; H = 3·6 per cent.

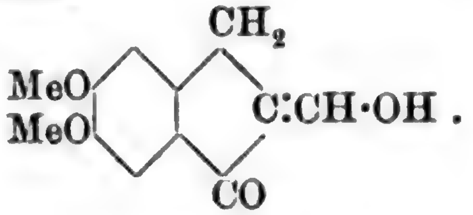
Attempt to Synthesise 7 : 4′ : 5′-*Trimethoxy*-4 : 3-*indenobenzopyranol* (1 : 4) *Anhydrohydrochloride* (p. 1149).

The first step in these synthetical experiments was the condensation of 5 : 6-dimethoxyhydrindone with formic ester, and this was carried out in the following way. Dimethoxyhydrindone (5 grams) was dissolved in 100 c.c. of light petroleum (b. p. about 110°), mixed with formic ester (12 grams), and then sodamide (10 grams) was gradually added to the hot solution. Each addition caused a vigorous reaction, and a drab sodium derivative separated. When all the sodamide had been added, the mixture was heated for half an hour on the water-bath, treated with ice, and the aqueous layer separated. The solution was acidified with hydrochloric acid, the yellow precipitate collected, drained on porous porcelain, and crystallised from ethyl acetate:

0·1314 gave 0·3145 CO_2 and 0·0652 H_2O. C = 65·3; H = 5·5.

$C_{12}H_{12}O_4$ requires C = 65·5; H = 5·4 per cent.

5 : 6-*Dimethoxy*-2-*hydroxymethylene*-1-*hydrindone* separates from acetic ester in yellow, prismatic needles, softens at 155°, and is completely melted at 170°. It dissolves in concentrated sulphuric acid with a cherry-red colour, and its alcoholic solution gives a green coloration with ferric chloride. Since it dissolves both in alkali carbonates and in sodium acetate, there can be no doubt but that it is a true hydroxymethylene compound, and that its constitution is represented by the formula

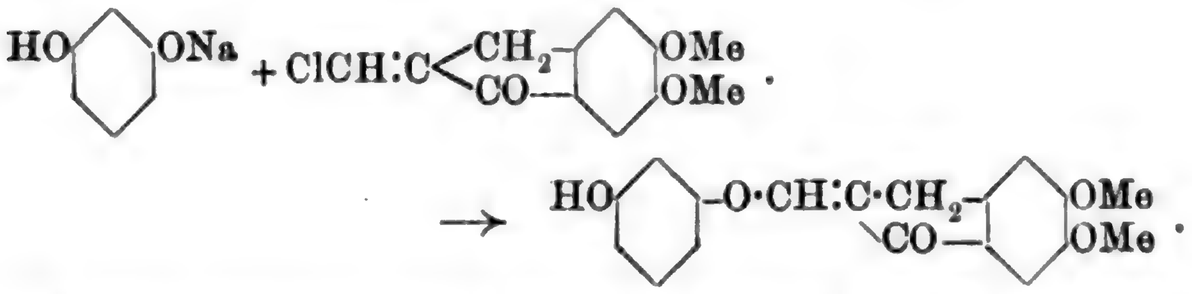


The next step was to replace the hydroxyl group by chlorine, and this was done by digesting the hydroxymethylene compound with phosphorus trichloride until solution was complete. The product was poured on to ice, and, when the excess of trichloride had been decomposed, the whole was extracted with ether, the ethereal solution washed with dilute sodium carbonate, dried, and the ether evaporated. The solid residue separated from ether in microscopic threads, and, after drying over sulphuric acid in a vacuum, the following result was obtained on analysis:

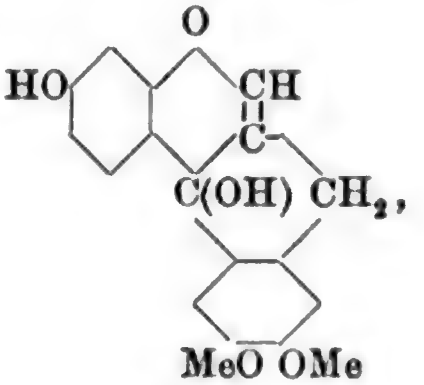
0·1309 gave 0·0781 AgCl. Cl = 14·6.

$C_{12}H_{11}O_3Cl$ requires Cl = 14·7 per cent.

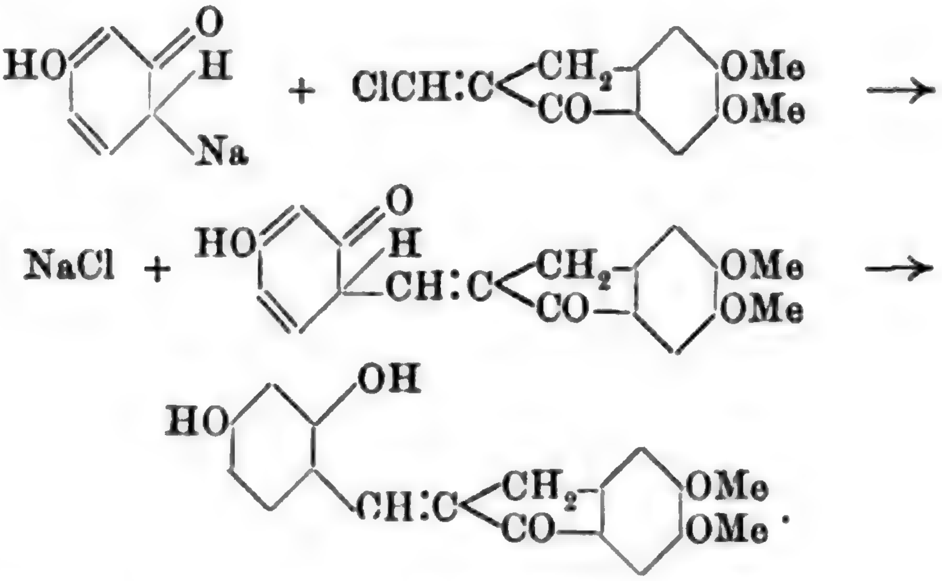
This chloro-derivative melts at 155°, and is clearly 5 : 6-*dimethoxy*-2-*chloromethylene*-1-*hydrindone*. We next proceeded to investigate the condensation of this substance with sodium resorcinol in the hope that the condensation would take place in accordance with the scheme:



The latter substance would doubtless undergo internal condensation when treated with acids to form a derivative of 4 : 3-indenobenzopyranol, namely,



and this on methylation and treatment with hydrochloric acid should yield the anhydrohydrochloride which has been obtained from tetramethyldihydrobrazileinol (p. 1149). Unfortunately, the condensation took place in a quite unexpected manner with the formation of 2′ : 4′-*dihydroxy*-5 : 6-*dimethoxy*-2-*benzylidene*-1-*hydrindone*, a substance which we had described in a previous paper (Trans., 1907, **91**, 1097). In this synthesis, the sodium derivative of resorcinol may be assumed to react in its tautomeric form, as if the sodium were attached to carbon, and the whole process is then readily explained by the following scheme :

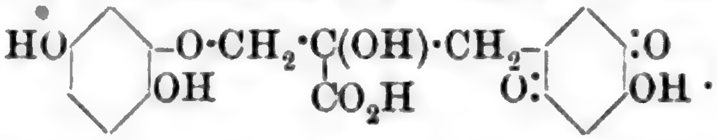


The following are the details of the experiment :

Resorcinol (1·1 grams) was dissolved in a little alcohol and mixed with a solution of sodium (0·3 gram) in alcohol ; the chloro-compound (2·4 grams) was then added and the solution boiled, when an orange-red colour gradually developed. After half an hour, the product was diluted with water, the pale brown, crystalline precipitate collected, and crystallised from alcohol. The pure substance decomposed at 235°, and showed all the reactions of 2′ : 4′-dihydroxy-5 : 6-dimethoxy-2-benzylidene-1-hydrindone. In order to be certain of its identity, we methylated the substance and obtained the corresponding tetramethoxy-derivative of melting point 189° (Trans., 1907, **91**, 1101).

The Action of Hydrogen Peroxide on Brazilein.

Formation of a : 4 : 2′ : 5′-*Tetrahydroxy-β′-phenoxy-β-2 : 5-quinoyl-isobutyric Acid,*



In preparing this quinone, brazilein (14 grams) is suspended in glacial acetic acid (130 c.c.), mixed with hydrogen peroxide (20 c.c. of 30 per cent.), and warmed to 30°. The temperature gradually rises to 38—40°, but, owing to the fact that brazilein is very sparingly soluble in acetic acid at this temperature, the reaction proceeds only slowly, and usually requires forty-five minutes for completion. After warming to 50°, the product is filtered,* and the deep brown filtrate allowed to stand overnight; the crystalline precipitate, which will have separated, is collected, washed with cold acetic acid until the filtrate is nearly colourless, and drained on porous porcelain. The beautiful dark brown, satiny mass is seen under the microscope to consist of transparent, brown needles and to be quite homogeneous. Three different specimens were analysed, the two first were obtained directly in the manner just described, and the third was recrystallised from acetic acid:

0·1788 gave 0·3623 CO_2 and 0·0625 H_2O. C = 55·3; H = 3·9.
0·1491 „ 0·3001 CO_2 „ 0·0540 H_2O. C = 55·0; H = 4·1.
0·1495 „ 0·2998 CO_2 „ 0·0552 H_2O. C = 54·8; H = 4·0.
$C_{16}H_{14}O_9$ requires C = 54·8; H = 4·0 per cent.

This quinone dissolves in boiling acetic acid, but more readily in formic acid, and separates, on cooling, in almost black, microscopic balls of needles. It dissolves in sodium carbonate or potassium hydroxide in the cold, yielding deep claret solutions quite different in appearance from the colour of the solutions of brazilein in alkalis.

It shows some very remarkable colour reactions, of which only the following need be mentioned. It dissolves in dilute ammonia with a reddish-brown colour, and the solution, when exposed to air, becomes brown, then an intense indigo-blue, and lastly deep violet.

If the solution in ammonia is shaken with zinc dust and rapidly filtered, a yellow solution is obtained, which in contact with air becomes an intense blue. An intense indigo-blue solution is also produced when a drop of sulphuric acid is added to a speck of the quinone dissolved in acetic acid. A trace of the quinone dissolves in concentrated sulphuric acid with a reddish-violet colour, this rapidly becomes bluish-violet, then indigo-blue, and gradually deep green, and, if the solution is now cautiously warmed, the green colour fades somewhat, becomes browner, and then deep violet.

---

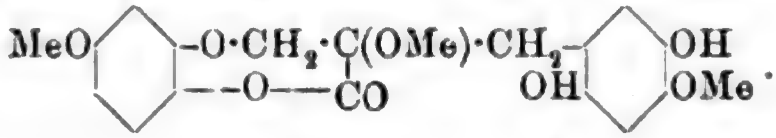
* When this preparation is successful, only about 4 grams of solid should remain undissolved, but, in some cases, a much larger quantity will have separated before filtration. This consists of quinone mixed with varying quantities of unchanged brazilein, and, if treated again with acetic acid and hydrogen peroxide, the brazilein will be readily oxidised and the precipitate is then almost pure quinone.

A note on this very effective method of oxidation was published by me in 1907 (Proc., **23**, 166) and thought to be new, but Prof. A. F. Holleman has kindly pointed out that he had employed the same conditions in 1904 (*Rec. trav. Chim.*, **23**, 169).—W. H. P., jun.

The quinone is readily reduced by alkaline reducing agents, such as sodium hydroxide and zinc dust, and, when boiled with acetic acid, zinc dust and acetic anhydride, reduction and acetylation take place simultaneously, and a colourless solution is formed which, when poured into water, deposits a voluminous, white precipitate. The investigation of this interesting product of reduction is not yet complete.

The Action of Hydrogen Peroxide on Trimethylbrazilein.

Formation of the Lactone of 2′ : 2 : 5-*Trihydroxy-α* : 4 : 5′-*trimethoxy-β-phenoxy-β-phenyl*isobut*yric Acid,*



When trimethylbrazilein (8 grams) is dissolved in warm glacial acetic acid (50 c.c.), well cooled, and mixed with 7 c.c. of 30 per cent. hydrogen peroxide, the colour of the solution becomes intensified, the temperature soon begins to rise, and the acetic acid ultimately boils. On cooling, the new lactone crystallises out. The best results are obtained by conducting the experiment in a wide test-tube provided with a thermometer and keeping the temperature at 40—45°, when, after about fifteen minutes, the dark brown liquid begins to crystallise and soon becomes semi-solid. The product is mixed with alcohol (3 vols.), the crystalline mass collected, washed with alcohol until quite free from the dark-coloured mother liquor, drained on porous porcelain, and recrystallised from boiling glacial acetic acid, from which it separates as a voluminous mass of almost colourless needles:

0·2147 gave 0·4800 CO_2 and 0·1036 H_2O. C = 61·0 ; H = 5·4.
0·1595 „ 0·3573 CO_2 „ 0·0760 H_2O. C = 61·1 ; H = 5·3.
$C_{19}H_{20}O_8$ requires C = 61·0 ; H = 5·4 per cent.

The determination of the methoxy-groups gave the following result:

0·1822 gave 0·3310 AgI. MeO = 24·3.
$C_{19}H_{20}O_8$, containing three MeO groups, requires MeO = 24·7 per cent.

This lactone melts at about 218—220°, but shrinks together a few degrees below this. It is sparingly soluble in hot alcohol, acetic acid, or formic acid, and almost insoluble in cold alcohol, benzene, or chloroform. It separates from its solution in boiling formic acid in beautiful colourless, glistening needles.

It is insoluble in cold dilute sodium carbonate, but, on warming, it dissolves, yielding an almost colourless solution, which, owing to oxidation, rapidly becomes brown and then purple; potassium hydroxide dissolves it in the cold with the same changes of colour, and the alkaline solutions give no precipitate with acids, showing that the hydroxy-acid is readily soluble in water. Towards acids the lactone is very stable, since it does not appear to be readily changed by boiling with concentrated hydrochloric acid or dilute sulphuric acid.

It dissolves in concentrated sulphuric acid with a reddish-violet colour, which soon changes to bluish-violet, and the addition of a drop of *iso*amyl nitrite causes the colour to become an intense blood-red.

When concentrated ferric chloride is added to a solution of the substance in hot acetic acid, a dark brown solution is produced, and the addition of water causes a brown, amorphous substance to separate. The hot acetic acid solution gives with *iso*amyl nitrite or concentrated sodium nitrite an intense brownish-orange solution, from which water precipitates a bright orange substance. Chromic acid rapidly oxidises the solution of the lactone in acetic acid, and a dark brown precipitate is formed, which quickly dissolves with a dark brown colour. When the lactone (2 grams), dissolved in excess of potassium hydroxide, is oxidised in a coal-gas atmosphere with hydrogen peroxide (2·5 c.c. of the 30 per cent. solution) at 40°, it is converted into a brown syrup, which is very soluble in water and gives an immediate precipitate with *p*-bromophenylhydrazine acetate.

One of the most remarkable properties of the lactone of melting point 218° is the fact that it may be distilled under reduced pressure. When 5 grams were rapidly heated in a small retort under 10 mm. pressure, a sublimate soon formed and then an oil distilled, which crystallised in the neck of the retort, only a comparatively small carbonaceous residue being left.

The distillate was melted on to a watch-glass and found to weigh 3 grams, and, when rubbed with alcohol, it yielded a mass of crystals which melted at 218°, and consisted of the unchanged lactone.

It is remarkable that a substance of such complicated structure and high molecular weight should distil.

The *acetyl* derivative.—The lactone of melting point 218° is sparingly soluble in cold acetic anhydride, but dissolves readily on warming, and if, after boiling for half an hour, the cold solution is poured into water, a resinous substance separates which, in contact with ice-water, soon becomes quite hard. The mass was ground up with water, collected, drained on porous porcelain, and crystallised from methyl alcohol, from which part of the substance usually separates as a gum, and the liquid then becomes filled with a mass of woolly balls or needles. Analysis showed that this substance is a *monoacetyl* derivative, instead of the diacetyl derivative which was to be expected:

0·1350 gave 0·2960 CO_2 and 0·0663 H_2O. $C = 59·8$; $H = 5·4$.
0·1260 „ 0·2753 CO_2 „ 0·0610 H_2O. $C = 59·6$; $H = 5·4$.
$C_{21}H_{22}O_9$ requires $C = 60·3$; $H = 5·3$ per cent.

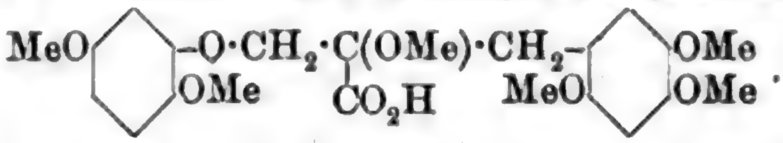
This acetyl derivative melts at 113—114°, and is readily soluble in alcohol or benzene, but sparingly so in light petroleum. It dissolves at once in cold dilute potassium hydroxide, yielding a colourless solution which, in contact with air, soon becomes brown.

*Formation of the Lactone of Trihydroxytrimethoxyphenoxyphenyl*iso*butyric Acid by the Action of Hydrogen Peroxide on Trimethyldihydrobrazileinol.*—In carrying out this experiment, trimethyldihydrobrazileinol (1 gram) suspended in acetic acid (10 c.c.) was mixed with 2 c.c. of hydrogen peroxide (30 per cent.), when the temperature rapidly rose and the substance dissolved, forming a deep brown solution. The temperature was kept at 45° until crystallisation set in, and in a short time the whole became solid enough to allow of the test-tube being inverted without loss. After collecting, washing with alcohol, and crystallising from this solvent, a mass of nearly colourless needles were obtained, which gave on analysis:

0·1935 gave 0·4320 CO_2 and 0·0936 H_2O. $C = 60·9$; $H = 5·3$.
$C_{19}H_{20}O_8$ requires $C = 61·0$; $H = 5·4$ per cent.

This substance melted at 218°, and was identical with the lactone obtained from trimethylbrazilein, since there was no alteration in melting point when the two specimens were mixed.

a : 2 : 4 : 5 : 2′ : 5′-*Hexamethoxy-β′-phenoxy-β-phenyl*iso*butyric Acid,*



The methyl ester of this acid is obtained from the lactone of melting point 218°, described in the last section, by treatment with potassium hydroxide and methyl sulphate under the following conditions.

The lactone (10 grams) is placed in a 1500 c.c. flask filled with coal gas, sufficient dilute potassium hydroxide is added to dissolve it, and then methyl sulphate and potassium hydroxide are added alternately with constant shaking until a crystalline precipitate separates, care being taken, by cooling, that the temperature does not rise above 40°. After standing for two hours, the precipitate is collected, washed well,* and crystallised from 70 per cent. methyl alcohol:

0·1628 gave 0·3660 CO_2 and 0·0985 H_2O. C = 61·3; H = 6·7.
0·1423 „ 0·3204 CO_2 „ 0·0864 H_2O. C = 61·4; H = 6·7.
$C_{23}H_{30}O_9$ requires C = 61·3; H = 6·7 per cent.

The determination of the methoxy-groups gave the following result:

0·2420 gave 0·8650 AgI. MeO = 47·2.
$C_{23}H_{30}O_9$, containing seven MeO groups, requires MeO = 48·2 per cent.

This *methyl* ester separates from dilute methyl alcohol in beautiful colourless prisms, like sugar crystals, and melts at 91°.

It is readily soluble in hot methyl or ethyl alcohols or acetic acid, but sparingly so in light petroleum. It dissolves in sulphuric acid with a yellow colour, which, on warming, becomes an intense brownish-green, and, if left overnight, a deep sage-green. It is very stable towards permanganate, even on warming.

The *hexamethoxy-acid.*—The methyl ester of this acid, just described, dissolves readily in warm methyl-alcoholic potash, but hydrolysis takes place slowly even on warming. After boiling for an hour with a large excess of concentrated methyl-alcoholic potash, water was added, the solution evaporated until free from methyl alcohol, cooled, and acidified, when a gum separated which, warmed with much water, rapidly solidified. The mass was ground with water, collected, and crystallised from dilute methyl alcohol, from which it separates in glistening, four-sided plates containing 1 molecule of water:

0·1813 gave 0·3864 CO_2 and 0·1104 H_2O. C = 58·2; H = 6·7.
0·1418 „ 0·3048 CO_2 „ 0·0880 H_2O. C = 58·6; H = 6·9.
0·2266 „ 0·4850 CO_2 „ 0·1393 H_2O. C = 58·4; H = 6·8.
$C_{22}H_{28}O_9,H_2O$ requires C = 58·2; H = 6·6 per cent.

When this acid is heated at 100°, it loses water, and is converted into a gum which, on exposure to air, gradually attracts moisture and becomes crystalline. This change takes place rapidly if the gum is rubbed with moist acetic ester. A determination of the water in the crystalline acid gave the following result:

---

* When the alkaline filtrate is acidified, a gummy substance sometimes separates, which, when warmed with water, gradually crystallises, and, after crystallisation from dilute methyl alcohol, melts at 100—102°, and consists of the pure hexamethoxy-acid.

0·4470, heated at 100° for 1½ hours, lost 0·0173, or 3·9 per cent.
$C_{22}H_{30}O_{10}$ losing H_2O corresponds with 4·0 per cent.

The methoxy-determination in the crystalline acid gave:

0·1740 gave 0·5490 AgI. MeO = 41·3.
$C_{22}H_{30}H_{10}$, containing six MeO groups, requires MeO = 41·0 per cent.

The hexamethoxy-acid, when rapidly heated, softens at about 95° and melts at 100—102°. When boiled with water, it dissolves appreciably, and crystallises from the filtered solution in colourless, thin, transparent, four-sided plates, which, when dry, have a satiny lustre. It dissolves readily in sodium carbonate, and the concentrated solution crystallises, owing to the separation of a sparingly soluble sodium salt; the solution of this salt is readily oxidised by permanganate. The molecular weight of the acid was controlled by titration with *N*/10 sodium hydroxide, when it was found that 0·3386 required for neutralisation about 0·032 NaOH, whereas this amount of a monobasic acid, $C_{22}H_{30}O_{10}$, should neutralise 0·029 NaOH. The *silver* salt was obtained by adding silver nitrate to a faintly alkaline solution of the ammonium salt as a white, chalky precipitate. It was washed with warm water and dried on porous porcelain over sulphuric acid:

0·3900 gave 0·0800 Ag. Ag = 20·5.
$C_{22}H_{27}O_9Ag$ requires Ag = 19·9 per cent.

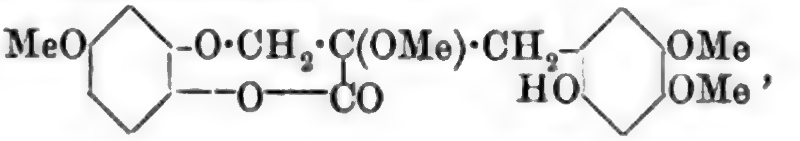
A slightly alkaline solution of the ammonium salt gives no precipitate with barium or calcium chlorides, but a very pale green precipitate with copper sulphate.

The oxidation of the acid by permanganate was repeatedly investigated under varying conditions in the hope that degradation products might be obtained which would conclusively prove the structure of the acid, but much oxalic acid was always formed, and no other acids could be isolated in sufficient quantity for examination.

The acid dissolves in fuming aqueous hydrobromic acid in the cold, yielding an almost colourless solution, which, on long standing, becomes a brilliant bluish-purple. It dissolves in sulphuric acid, and the greenish-brown solution gradually becomes quite black; when poured into water, a black precipitate separates, and the liquid has a strong odour of sulphur dioxide.

The Action of Hydrogen Peroxide on Tetramethyldihydrobrazileinol.

Formation of the Lactone of 2′ : 2-Dihydroxy-α : 4 : 5 : 5′-tetramethoxy-β′-phenoxy-β-phenylisobutyric Acid,



and its Conversion into the Methyl Ester of α : 2 : 4 : 5 : 2′ : 5′-Hexamethoxy-β′-phenoxy-β-phenylisobutyric Acid.

In order to prepare the above lactone, tetramethyldihydrobrazileinol (p. 1140), in quantities of 1 gram, is dissolved in acetic acid (3 c.c.), mixed with 1 c.c. of hydrogen peroxide (30 per cent.), and the temperature kept at about 40°. The pink colour of the solution gradually becomes paler, crystallisation soon commences, and in a short time the mass solidifies. After collecting and washing with a little acetic acid, the substance is readily purified by recrystallisation from alcohol:

0·1794 gave 0·4047 CO_2 and 0·0920 H_2O. C = 61·5 ; H = 5·7.
0·1614 „ 0·3636 CO_2 „ 0·0828 H_2O. C = 61·4 ; H = 5·7.

$C_{20}H_{22}O_8$ requires C = 61·5 ; H = 5·6 per cent.

The following determination of the methoxy-groups was made:

0·1318 gave 0·3120 AgI. MeO = 31·2.

$C_{20}H_{22}O_8$, containing four MeO groups, requires MeO = 31·7 per cent.

This lactone crystallises from alcohol in groups of almost colourless needles and melts at 160°. It is insoluble in cold dilute sodium carbonate, but dissolves readily on warming; it is at once soluble in cold dilute potassium hydroxide. These alkaline solutions differ from those of the lactone of the 2′ : 2 : 5-trihydroxy-α : 4 : 5′-trimethoxy-acid (m. p. 218°) (p. 1157) in that they are only very slowly turned brown on exposure to air, and also, when acidified, they yield a solid substance which, since it is immediately soluble in cold sodium carbonate, is probably the corresponding hydroxy-acid. The lactone gives with sulphuric acid the colour changes described in the case of the lactone of melting point 218°.

Conversion of the Lactone (m. p. 160°) *into the Methyl Ester of Hexamethoxy-β′-phenoxy-β-phenylisobutyric Acid.*

In carrying out this experiment, the lactone was dissolved in excess of dilute potassium hydroxide, and shaken with methyl sulphate and potassium hydroxide until a crystalline substance separated. This was collected and recrystallised from dilute methyl alcohol, when colourless prisms were obtained which gave, on analysis, the following results:

0·1304 gave 0·2928 CO_2 and 0·0792 H_2O. C = 61·2; H = 6·7.

$C_{23}H_{30}O_9$ requires C = 61·3; H = 6·7 per cent.

This substance melted at 91—92°, and was identical with the methyl ester described on p. 1159, since, when the two specimens were mixed, there was no alteration in melting point.

During the course of these two investigations, much of the heavy expense has been met by repeated Grants from the Royal Society and from the Chemical Society, and the authors wish to express their thanks for this valuable assistance. They also wish to thank Mr. W. N. Haworth, M.Sc., for valuable assistance, especially in connexion with the analytical work.

THE UNIVERSITY,
MANCHESTER.

CXII.—*The Interaction of Copper and Nitric Acid in Presence of Metallic Nitrates Considered with Reference to the Existence of Hydrates in Solution.*

By EDWARD HENRY RENNIE, M.A., D.Sc., ALFRED J. HIGGIN, F.I.C., and WILLIAM TERNENT COOKE, D.Sc.

SOME years ago, one of us was consulted by the Broken Hill Proprietary Company in a disputed patent case in which one of the points at issue was whether the action of dilute sulphuric acid on zinc-lead concentrates would be essentially modified by the addition of sodium sulphate. In support of the contention that there would be a modification, a demonstration was given in which equal quantities of the concentrates having been placed in two beakers, diluted nitric acid was added to the one and to the other an equal volume of the same acid saturated with sodium nitrate, the temperature of both being the same. Action commenced much earlier and proceeded much more rapidly in the case in which sodium nitrate had been added. The explanation at first suggested was that the sodium nitrate was impure and that it contained something which accelerated the action of the nitric acid. On roughly testing the nitrate, however, it appeared to be fairly pure and further experiments were decided on. The concentrates being rather awkward material to deal with, metallic copper was substituted. It was found that the copper dissolved much more rapidly in nitric acid containing sodium nitrate than in the acid alone. An experiment was then tried with potassium nitrate, but no similar acceleration was observed. This led to a suspicion that the first idea of the presence of impurity in the sodium nitrate must be the correct one; to test this, several specimens of purified sodium nitrate were prepared in various ways:

(*a*) By repeated crystallisation of commercially pure nitrate.
(*b*) By neutralising Merck's pure sodium hydroxide with nitric acid.
(*c*) By neutralising pure sodium hydrogen carbonate with nitric acid.

All the samples were crystallised until fairly strong solutions were free from chlorine, iron, sulphuric acid, and nitrous acid; nor could any chlorate or iodate be detected in them. The result was the same with all the samples. Moreover, it was shown by direct experiment that small quantities of iron, sulphuric acid, chlorates or perchlorates had no accelerating effect (chlorates distinctly retarded the action). Even traces of nitrites had no appreciable effect, although on increasing the quantity acceleration set in. Further experiments showed, moreover, that the acceleration increased with the quantity of nitrate added but tended towards a maximum. It was then determined to carry out a systematic investigation.

An apparatus was so constructed that two test-tubes, each about one inch in diameter and six inches in length, could be placed side by side and partly immersed in a beaker of water, which was fitted with a thermo-regulator. The two stirrers were made by flattening out the ends of two glass rods and then twisting the flattened ends into the form of screws; these were fixed in a movable frame, so that they could be simultaneously immersed in the two tubes and made to revolve at exactly the same rate by means of a small water turbine. The temperature in all experiments was 59° (any temperature near 60° was found convenient as regards the time required to effect dissolution) and was easily kept constant within half a degree by means of an ordinary gas regulator (it was ascertained that small variations of temperature were of no importance). Pure electrolytic copper foil was used. The method of operating was as follows:

Into each test-tube was poured from a burette a known volume (in most cases 10 c.c.) of nitric acid of suitable dilution, with or without a weighed quantity of nitrate; the tubes were placed in the water-bath so that they were immersed and time was given for the contents to acquire the temperature of the bath; two pieces of copper of the same weight and superficial area were dropped simultaneously one into each tube and the stirrers were inserted and set in motion, the time of dropping in the copper being then noted and also the time at which it was completely dissolved. This could easily be observed through the clear water in the beaker. The copper used was cut into pieces of the size required, washed successively with ether, alcohol and distilled water, dried as far as possible between sheets of clean blotting paper and finally dried by gently warming in the air; it was placed in a well-closed bottle and was never handled by the fingers; its surface remained perfectly bright. In all the experiments, the pieces of copper rotated in the tubes, owing to the action of the stirrers. It was found that by operating in this way fairly concordant results could be obtained but there were some irregularities. In the first place, as might have been expected from the work of Veley (*Proc. Roy. Soc.*, 1889, **46**, 216) on the action of nitric acid on copper, the rate of stirring was found to affect the rate of dissolution. By extremely rapid stirring, the time required for dissolution could be considerably prolonged but by regulating the stirring at the same moderate rate for each experiment, as nearly as could be judged by the eye (by watching a mark on the small band connecting the stirrers with the motor), fairly concordant results could be obtained, the copper being dissolved within a moderate time. Again, under exactly similar conditions in the two tubes, the copper almost invariably dissolved in one slightly faster than in the other, this being specially noticeable when the times were longer. This was traced to a difference in the stirrers, for on reversing the stirrers the effect was reversed. The difference, however, did not affect the general result. Occasionally a piece of copper would behave abnormally and take very much longer than the average time to dissolve. We could only suppose that this was due to some abnormality of surface, possibly imperfect cleansing, which delayed the action. In spite of these drawbacks, however, the figures agree sufficiently well for our purpose. In the earlier experiments, the weight of copper used varied only in extreme cases from 0·095 to 0·098 gram (the great majority varied only from 0·096 to 0·097), the superficial area in each case being practically the same. The nitric acid used was prepared by diluting to 1 litre 100 c.c. of 65·68 per cent. nitric acid. It therefore contained approximately 6·5 per cent. In each experiment, 11 c.c. were taken; the temperature was maintained at 59°.

The following are some results obtained with sodium nitrate, the vertical column giving the time of complete dissolution to the nearest half minute. At the head of each column after the first is placed the weight, in grams, of dry sodium nitrate added. Abnormal results, which occurred extremely rarely (three or four in the whole of the experiments contained in this paper) are omitted:

Results with Sodium Nitrate.

Nitric acid alone.	0·5	1·0	2·0	4·0	5·0	6·0	8·0	10·0
48	40·5	38·0	31·0	24·0	18·0	17·0	12·5	13·5
49	44·0	37·0	31·0	28·0	18·0	17·0	13·0	13·5
49	43·0	40·0	30·0	23·0	18·5	16·0	13·0	13·0
48	49·0	38·5	33·0	24·5	20·0	16·5	13·5	13·6
49	42·5	37·0	35·5	26·0	20·5	16·5	—	—
46	42·0	29·0	34·0	22·0	18·5	16·0	—	—
47	41·5	37·0	—	—	19·5	—	—	—
49	43·0	41·0	—	—	—	—	—	—

A limit is apparently reached on the addition of 8 grams of nitrate.

As previously stated, potassium nitrate appeared to have no accelerating effect. The following table gives results with potassium nitrate, the conditions being the same as with the sodium salt. The potassium nitrate was repeatedly recrystallised until pure:

Results with Potassium Nitrate.

0·5	1·0	2·0	4·0	6·0
47·5	44·5	48·0	52·0	42·5
49·0	45·0	44·0	51·0	57·0
46·0	47·5	47·0	51·5	52·5
45·0	49·0	50·0	49·5	50·0
48·5	46·0	48·0	51·5	—

If anything, potassium nitrate in large quantities produces a slight retardation.

Preliminary experiments having shown that other nitrates produced effects similar to those due to sodium nitrate, a fresh series was instituted, using equivalent weights of the various nitrates so as to compare their effects. In all the following experiments, the pieces of copper weighed 0·0775 gram within 0·0005 gram, their superficial area being as nearly as possible 1·96 square cm. The nitric acid used was 2*N*. In each experiment, the quantity of acid taken was 10 c.c. and the amount of nitrate added was 0·01, 0·02, 0·03, &c., of the equivalent weight in grams.

The following series of experiments was made with sodium nitrate in order to establish a standard of comparison for other nitrates:

Nitric acid alone.	0·01 equiv.	0·02 equiv.	0·03 equiv.	0·04 equiv.	0·06 equiv.	0·1 equiv.	0·12 equiv. did not all dissolve.
32·0	21·0	16·0	12·5	11·0	10·0	8·5	8·0
33·0	22·0	17·5	13·5	12·5	10·5	9·0	8·5
32·5	21·5	17·5	14·5	13·5	10·5	—	—
34·5	23·5	18·5	15·5	12·0	11·0	—	—
32·5	22·0	17·5	13·5	10·5	—	—	—
33·5	24·0	18·5	14·0	12·0	—	—	—
34·0	23·0	17·5	13·5	12·5	—	—	—
33·0	24·0	18·0	14·0	13·0	—	—	—
Mean.	Mean.	Mean.	Mean.	Mean.	Mean.	Mean.	Mean.
33·1	22·4	17·5	14·0	12·1	10·7	8·7	8·2

Further experiments were not made with potassium nitrate, the results previously given being sufficient to show that potassium nitrate has no accelerating but rather a slightly retarding effect.

Lithium Nitrate.—The purest obtainable lithium carbonate was dissolved in nitric acid, the solution evaporated to dryness, dissolved in alcohol, evaporated to dryness, heated to 110—120° and preserved in a well-closed bottle. That it was practically pure was shown by the fact that on conversion into sulphate it yielded an almost theoretical result. No special examination was made for traces of impurity, it having been shown already that such traces have little or no effect. The following results show that lithium nitrate has a much greater accelerating effect than sodium nitrate:

0·01 equiv.	24·0	24·0	24·0	26·0	—
0·02 equiv.	9·5	9·5	11·0	10·0	10·0
0·03 equiv.	5·0	5·5	5·0	5·5	—

Rubidium Nitrate.—The rubidium nitrate used was a well-crystallised specimen obtained from Merck and was not specially examined; its solution in water was quite neutral. As the quantity available was small, the solutions once used were freed from copper by electrolysis, evaporated, crystallised and used again. The results were as follows:

0·02 equiv.	37·0	38·5	—	—	—
0·03 equiv.	41·5	40·0	51 (?)	46	48
0·05 equiv.	53·5	55·0	—	—	—

Caesium Nitrate.—There marks made with respect to the condition of the rubidium salt apply also to the cæsium nitrate. The effect of this salt was as follows:

0·02 equiv.	43·5	41	47	55 (?)	48
0·03 equiv.	50·0	57	57	—	—

These results are obviously not so concordant as those obtained in other cases. It is evident, however, that both rubidium and cæsium nitrates effect a marked *retardation* and that the retardation is greater with the cæsium than with the rubidium salt. During these latter experiments and frequently during the whole of the work, the nitric acid was tested by itself and found to give a uniform rate of dissolution.

Calcium Nitrate.—The calcium nitrate used was prepared by dissolving pure precipitated calcium carbonate in nitric acid, evaporating to dryness and drying at about 120°. The results obtained were:

0·02 equiv.	14	14·5	15	15
0·03 equiv.	9	9·0	—	—

Acceleration is evidently greater but not so great as with magnesium nitrate (see below).

Strontium Nitrate.—The strontium nitrate was thoroughly purified by recrystallising commercially pure material and was free from any appreciable amount of impurity. It was rendered anhydrous before using by heating to 110—120°. Numerous experiments were made with this salt:

0·01 equiv.	26·5	25·5	28·5	29·0	25·0	27·0	27·0	29·0
0·02 equiv.	20·0	22·0	21·0	21·0	20·0	19·5	20·0	21·0
0·03 equiv.	14·0	14·0	15·0	16·0	14·0	14·0	15·0	15·5
0·04 equiv.	11·0	10·5	10·0	9·5	—	—	—	—

The acceleration is great but not so great as with calcium nitrate.

Barium Nitrate.—The solubility of barium nitrate in nitric acid is so small that no satisfactory result can be obtained with it. Even with nitric acid of half the strength used in these experiments, 0·01 equivalent of barium nitrate could not be dissolved in 10 c.c. With so much as could be dissolved, no accelerating effect could be detected.

Experiments with Nitrates of Magnesium, Zinc and Cadmium.—These being all very deliquescent salts, the method of operating with them was varied. In each case the pure oxide was prepared: the magnesium oxide by strongly igniting some specially prepared and purified carbonate; the zinc oxide by thoroughly washing and igniting commercial pure zinc oxide which had been used for analytical purposes, the freedom of which from all, but slight, traces of impurity was known; the cadmium oxide by precipitating cadmium sulphate with ammonium carbonate, washing thoroughly and igniting at a high temperature. The required weight of oxide was then mixed with exactly the quantity of nitric acid required to form the normal nitrate and the volume made up with a sufficient excess of nitric acid and water to make the solution $2N$ with respect to the acid. Ten c.c. of this solution were then used for each experiment. This is obviously not quite the same thing as adding the required quantity of nitrate to 10 c.c. of $2N$ acid but the results obtained with these three nitrates are at least comparable among themselves and, considering the variations of time due to the conditions of experiments, are fairly comparable with those obtained in other cases. The results obtained with magnesium nitrate were:

0·01 equiv.	13·5	13·0	14·0	13·5	15·0	13·5	16·0	16·5
0·02 equiv.	5·5	5·5	6·0	6·0	5·5	6·0	—	—

There is a great acceleration, considerably greater than with lithium or calcium nitrate.

Zinc nitrate gave the following figures:

0·01 equiv.	15·5	16	16·0	17	15	17·0
0·02 equiv.	7·0	7	7·0	7	7	7·5
0·03 equiv.	4·0	5	4·5	4	4	4·5

The acceleration is not quite so great as with magnesium nitrate. With cadmium nitrate the results were:

0·01 equiv..........	15·0	17·0	15·5	18·5
0·02 equiv..........	8·0	8·5	8·5	—

The acceleration is slightly less than with zinc nitrate.

Experiments with Copper Nitrate.—The fact that the interaction of copper and nitric acid is in some way auto-accelerated has been frequently observed; the fact has been ascribed by Veley (*loc. cit.*) and others to the accumulation of nitrous acid in the solution. That the accumulation of nitrous acid is one factor in the acceleration need not be disputed, in fact, it appears evident from Veley's work; but that there is another factor operative, namely, the accumulation of copper nitrate, seems evident from the experiments now described.

Ordinary metallic copper was dissolved in nitric acid and the solution evaporated to crystallising point, taking care to keep an excess of nitric acid present to prevent formation of basic salt. The crystallised salt was separated, washed with ice-cold water and drained on a porous tile. It was redissolved and the solution again evaporated to crystallising point with sufficient acid to prevent the formation of basic nitrate. The crystals were well washed with ice-water, drained on a porous tile, placed for two or three days in a partly exhausted desiccator over sulphuric acid and then stored in a well-stoppered bottle.

The salt so obtained dissolved to a perfectly clear solution in water; the solution was very slightly acid to litmus paper. It contained 27·55 per cent. of copper, equivalent to 81·26 per cent. of anhydrous copper nitrate. Quantities of this preparation, corresponding to the required quantity of anhydrous nitrate, were then taken and made up with sufficient nitric acid and water to form a solution $2N$ with respect to the acid; 10 c.c. of the solution were taken for each experiment. The results were:

0·01 equiv.	17·0	17·0	16·5
0·02 equiv.	8·5	8·5	8·5

There is evidently great acceleration.

Experiments with Lead Nitrate.—The lead nitrate used was prepared by twice crystallising the commercially pure salt and heating it to 110—120°. Its solution in water was distinctly but not strongly acid; it was found just possible to dissolve 0·02 gram-equivalent in 10 c.c. of the acid at the temperature of the experiment. The following numbers were obtained:

0·02 equiv.	24	25	26

Evidently there is acceleration but less than with any nitrate tried which gives acceleration at all.

Experiments with Ammonium Nitrate.—A few experiments were tried with ammonium nitrate but the results, as was anticipated, were irregular and unsatisfactory. This is no doubt due to the effect of the ammonium salt on the nitrous acid produced.

Discussion of Results.

The fact that the hydrolytic effects of acids are considerably increased by the addition of their salts has been frequently noticed, especially in recent years; indeed, Caldwell points out (*Proc. Roy. Soc.*, 1907, **78**, *A*, 277) that as long ago as 1862 Löwenthal and Lenssen made experiments on the effect of salts on the rate of inversion of sucrose by acids and ascribed the acceleration they observed to the withdrawal of water from the salts and the consequent increase of strength of the acids. Quite recently the question has been taken up experimentally by H. E. Armstrong in conjunction with Caldwell, Whymper and Watson (*Proc. Roy. Soc.*, 1907, **79**, *A*, 576). Whymper more especially has examined the effect of the addition of nitrates on the sucroclastic effects of nitric acid. All these authors come to the same conclusion as Löwenthal and Lenssen; they find that the degree of hydration of various salts calculated from their experiments agrees fairly well with that determined by other experimenters by other methods. The experiments described in this paper seem to us to afford strong qualitative evidence in favour of the views now generally accepted as to the combination of solute with solvent. They appear, moreover, to supply evidence of a kind not hitherto published so far as we are aware. Armstrong and Watson, in their paper (*loc. cit.*), say: "As the substances in a solution share the solvent and *are in competition*, it is to be expected that hydration values will be found to vary from case to case and that it will not always be possible to approximate to the true [de]hydrating effect of a salt; indeed, cases are known in which salts *apparently retard hydrolysis.*" The italics are ours.

Our experiments with rubidium and cæsium nitrates afford strong evidence of considerable retardation of the action of nitric acid on copper, and those with potassium nitrate furnish some evidence in the same direction. It seems probable also that when a nitrate is added to dilute nitric acid, there is competition between the acid and water, both combining with the salt. We venture to think that the experiments with the nitrates of the alkali metals strongly support such a view, showing as they do that there is a decreasing acceleration from lithium nitrate to potassium nitrate, the latter producing not only no acceleration but a slight retardation, whilst an increasing retardation is noticeable from potassium nitrate to cæsium nitrate. It is both noteworthy in this connexion and probably significant that Ditte long ago (*Compt. rend.*, 1879, **89**, 576, 641) showed that potassium and rubidium are capable of forming acid nitrates (he apparently did not experiment with cæsium nitrate) but that lithium and sodium are not. With magnesium, calcium, and strontium nitrates, a similar decrease in acceleration is observed in the order named; owing to the insolubility of barium nitrate, nothing could be done with this salt. So far as they go, zinc and cadmium nitrates exhibit the same phenomenon. If these views are correct, then in the experiments carried out by H. E. Armstrong and his co-workers the same influence must have come into play as between the salt, acid, and water but the effects would be modified by the fact that they used acid of only half the strength used by us and that there were other substances present which themselves tended to combine either with the nitric acid, water, or acid. Moreover, the only salt they used which with us exhibited any retarding effect and that a very slight one was potassium nitrate; they did not experiment with rubidium or cæsium nitrates. It would be interesting to know whether the latter salts would exert any retarding influence on the inversion of sucrose by nitric acid. Qualitatively, our results accord with those of other observers if we consider the effects produced by *gram-molecular weights, not equivalents* of the nitrates, the order of acceleration being what it should be if the calculated hydration results are correct.

A further deduction to be drawn from these experiments which is implied in what has been already stated is that in any one group of metals the hydration of the nitrates in solution in dilute nitric acid decreases as the atomic weight of the metals increases, and, moreover, in the same order.

The action of copper nitrate has been discussed already.

Summary.

1. The dissolution of copper in nitric acid may be greatly accelerated by the addition of certain metallic nitrates.
2. Certain nitrates, however, such as those of cæsium and rubidium, retard the dissolution.
3. These phenomena are probably due to the withdrawal of water or nitric acid from the solution by the salt.

4. The acceleration decreases with nitrates of any one group of metals as the atomic weight increases and in the same order.

5. Copper nitrate has a great accelerating effect: therefore the auto-acceleration observed when copper is dissolved in nitric acid must be partly due to the copper nitrate formed.

6. These results afford additional evidence that the process of solution is accompanied by the combination of the solute with the solvent.

It is proposed to extend this inquiry in various direction, especially with a view to obtaining, if possible, retarding effects with other metals, acids and salts, in the hope also of so improving the method as to arrive at quantitative results.

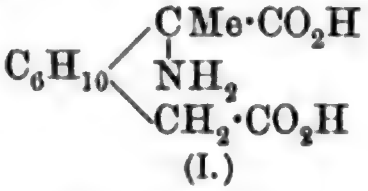
THE UNIVERSITY OF ADELAIDE.

CXIII.—*Condensation Products from Aminopinenedicarboxylic Acid.*

By WILLIAM GODDEN, B.Sc.

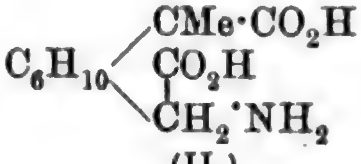
AT the conclusion of a paper on the amino-acid derived from pinene (Tilden and Blyther, Trans., 1906, **89**, 1563), it was mentioned that this compound is capable of forming certain condensation products. At the request of Professor Tilden, I undertook the further investigation of the subject, with the following results.

It may be observed that, of the two formulæ possible for this compound,



$$C_6H_{10}\begin{cases}\mathrm{CMe\cdot CO_2H}\\ \mathrm{NH_2}\\ \mathrm{CH_2\cdot CO_2H}\end{cases}$$

(I.)



$$C_6H_{10}\begin{cases}\mathrm{CMe\cdot CO_2H}\\ \mathrm{CO_2H}\\ \mathrm{CH_2\cdot NH_2}\end{cases}$$

(II.)

(Tilden and Burrows, Trans., 1905, **87**, 344), the latter appears to be the more probable, as the acidity of the acid is strongly marked, and when heated it readily evolves carbon dioxide.

An attempt to estimate quantitatively the amount of carbon dioxide produced by heating the acid to the melting point, and absorbing the evolved gas by means of potassium hydroxide, resulted in the collection of 42 parts of carbon dioxide from 229 parts, or one molecular proportion, of the acid. This corresponds therefore with the destruction of one carboxyl group. The residual substance, however, is dark-coloured and viscid, and it has not been found possible to characterise it.

If the acid is heated to fusion for a shorter time, auto-condensation of the acid seems to occur. A crystalline mass is left on cooling, from which, after removal of the uncrystallisable matter and recrystallisation from alcohol, melts and decomposes at 263°. On analysis, it gave the following results:

Found: C = 58·60, 58·60, 58·40; H = 8·98, 8·40, 8.30; N = 6·34, 6·75.

$C_{11}H_{19}O_4N$ requires C = 57·64; H = 8·30; N = 6·13 per cent.

On comparison of these numbers with those required by the formula of the amino-acid, it will be seen that there is only a slight difference in the carbon. The assumption that two molecules of the acid have interacted with loss of one molecule of water leads to a formula which requires 60·0 per cent. of carbon. The nearest approach to the composition found is provided by a formula which results from the coalescence of three molecules of the acid with loss of one molecule of water. This requires C = 59·1; H = 8·2; and N = 6·2 per cent. On the whole, however, it seems more probable that the substance is merely a kind of salt formed by the union of two or more molecules of the acid in virtue of its amphoteric character, and that, by recrystallisation, the original acid is gradually regenerated. This view is supported by the fact that it gives with sodium hydroxide and dilute copper sulphate solution a bluish-violet coloration practically identical with that which is produced by the original acid.

(1) *Condensation with Glycine.*

Molecular proportions or 5 grams of the amino-acid hydrochloride and 1·4 grams of glycine were mixed together and heated with 30 c.c. of absolute alcohol in a sealed tube at 110—120° for four hours. No pressure was observed. The clear alcoholic liquid was allowed to evaporate slowly to dryness, and a sticky, white solid separated. This was dissolved in water, neutralised with sodium hydroxide, and shaken with ether. The ether extracted nothing, but from the aqueous solution, on standing, colourless needles, melting at 234—236°, were deposited. On analysis:

Found: N = 9·7, 9·6.

$C_{13}H_{22}O_5N_2$ requires N = 9·8 per cent.

Condensation of one molecule of glycine and one molecule of the amino-acid had thus evidently taken place.

On mixing a hot aqueous solution of the substance with a hot solution of copper acetate, and leaving the mixture to cool, small, bluish-violet needles of the copper hydrogen salt separated. On analysis:

Found: Cu = 10·4, 10·3.

$C_{26}H_{42}O_{10}N_4Cu$ requires Cu = 10·03 per cent.

By suspending the substance in dry ether and passing in dry hydrogen chloride, a *hydrochloride* was produced. This was crystallised from water, and the chlorine estimated by titration with standard nitrate solution.

Found : Cl = 11·6, 11·3.

$C_{13}H_{22}O_5N_2,HCl$ requires Cl = 11·0 per cent.

(2) *Condensation with Aspartic Acid.*

Molecular proportions or 5 grams of the amino-acid hydrochloride and 2·5 grams of aspartic acid were mixed together and heated with 30 c.c. of absolute alcohol in a sealed tube at 110—120° for four hours. The solution, after being filtered from some deposited aspartic acid, was allowed to evaporate. The crystals obtained were dissolved in water, neutralised with sodium hydroxide, and, on standing, colourless needles were deposited.

Found : N = 7·6, 7·4.

$C_{26}H_{41}O_{10}N_3$ requires N = 7·58 per cent.

The condensation of one molecule of aspartic acid with two molecules of the amino-acid had thus taken place with elimination of two molecules of water.

The residue of unchanged aspartic acid is thus accounted for.

This substance gave a *copper* salt when a hot aqueous solution was mixed with a hot solution of copper acetate. On cooling, bluish-violet needles were deposited.

Found : Cu = 10·34, 10·43.

$C_{26}H_{39}O_{10}N_3Cu$ requires Cu = 10·31 per cent.

Condensation of the amino-acid with benzaldehyde appeared to occur when the two substances were heated together, but the product was uncrystallisable. With anthranilic acid no change seemed to take place.

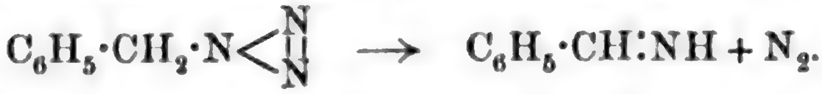
ROYAL COLLEGE OF SCIENCE, LONDON,
SOUTH KENSINGTON, S.W.

CXIV.—*The Triazo-group. Part IV. Allylazoimide.*

By MARTIN ONSLOW FORSTER and HANS EDUARD FIERZ.

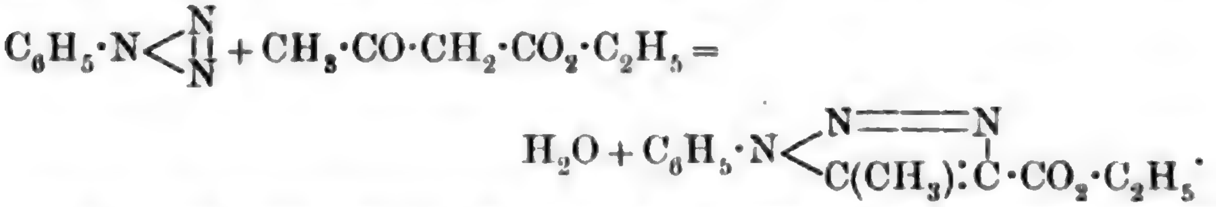
ATTENTION has been directed at various times to the facility with which the atoms composing the triazo-group part company, as testified by the following illustrations.

Benzylazoimide is resolved by acids into benzylideneimine and nitrogen (Curtius and Darapsky, *J. pr. Chem.*, 1901, [ii], **63**, 428):



$$C_6H_5\cdot CH_2\cdot N{<}\begin{array}{c}N\\ \|\\ N\end{array} \longrightarrow C_6H_5\cdot CH{:}NH + N_2.$$

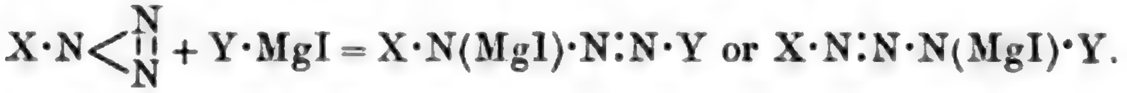
Phenylazoimide under the influence of sodium ethoxide may be condensed with numerous esters, yielding triazole derivatives (Dimroth, *Ber.*, 1902, **35**, 1029, 4041; *Annalen*, 1904, **335**, 1):



$$C_6H_5\cdot N{<}\begin{array}{c}N\\ \|\\ N\end{array} + CH_3\cdot CO\cdot CH_2\cdot CO_2\cdot C_2H_5 =$$

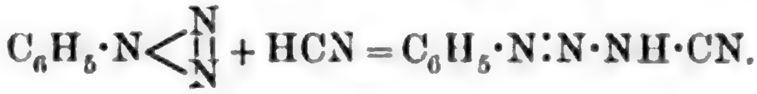
$$H_2O + C_6H_5\cdot N{<}\begin{array}{l}N{=\!=\!=}N\\ C(CH_3){:}C\cdot CO_2\cdot C_2H_5\end{array}.$$

Alkyl- and aryl-azoimides are transformed into diazoamino-compounds by the action of organo-magnesium derivatives (Dimroth, *Ber.*, 1903, **36**, 909; 1905, **38**, 670; 1906, **39**, 3906):



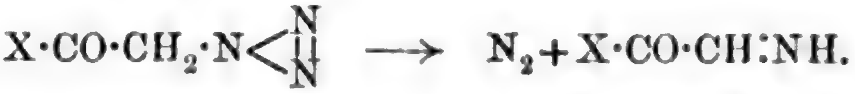
$$X\cdot N{<}\begin{array}{c}N\\ \|\\ N\end{array} + Y\cdot MgI = X\cdot N(MgI)\cdot N{:}N\cdot Y \text{ or } X\cdot N{:}N\cdot N(MgI)\cdot Y.$$

Potassium cyanide converts phenylazoimide into benzeneazocyanamide (Wolff and Lindenhayn, *Ber.*, 1904, **37**, 2374):



$$C_6H_5\cdot N{<}\begin{array}{c}N\\ \|\\ N\end{array} + HCN = C_6H_5\cdot N{:}N\cdot NH\cdot CN.$$

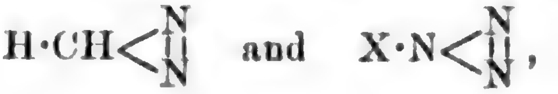
A trace of sodium ethoxide liberates two-thirds of the nitrogen from triazo-ketones (Forster and Fierz, Trans., 1905, **87**, 826; this vol., pp. 72 and 669):



$$X\cdot CO\cdot CH_2\cdot N{<}\begin{array}{c}N\\ \|\\ N\end{array} \longrightarrow N_2 + X\cdot CO\cdot CH{:}NH.$$

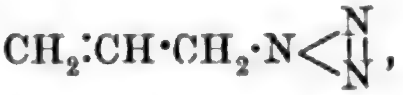
As an explanation of the last-named change, it has been suggested that, prior to elimination of nitrogen, the carbonyl group becomes saturated by the triazo-group, giving rise to an unstable cycloid which forthwith collapses.

The foregoing considerations, coupled with certain points of resemblance between diazomethane and the triazo-group,



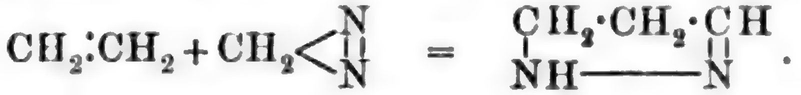
$$H\cdot CH{<}\begin{array}{c}N\\ \|\\ N\end{array} \quad \text{and} \quad X\cdot N{<}\begin{array}{c}N\\ \|\\ N\end{array},$$

led us to investigate the properties of allylazoimide, in which compound,



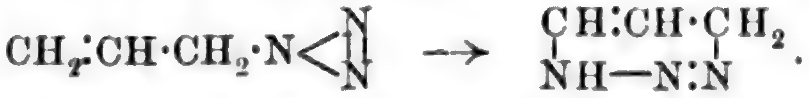
$$CH_2{:}CH{\cdot}CH_2{\cdot}N{<}\begin{smallmatrix}N\\ \|\\ N\end{smallmatrix},$$

one might anticipate the display of some attraction on the part of the ethenoid linking for the highly active triazo-group; given a suitable environment, there should occur redistribution of affinities analogous to the interaction of ethylene and diazomethane, of which the outcome is pyrazoline (Azzarello, *Atti R. Accad. Lincei*, 1905, [v], **14**, ii, 285):



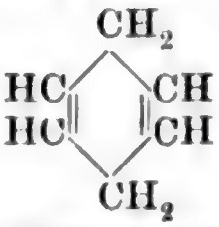
$$CH_2{:}CH_2+CH_2{<}\begin{smallmatrix}N\\ \|\\ N\end{smallmatrix} \; = \; \begin{matrix}CH_2{\cdot}CH_2{\cdot}CH\\ NH\text{———}N\end{matrix}.$$

On attempting to prepare allylazoimide from sodium azide and allyl chloride or iodide, interaction took place with moderate readiness, but it was noticed that, unless quickly removed, the triazo-derivative undergoes a profound change, in consequence of which we have never obtained yields exceeding 30 per cent. This is explained by the fact that allylazoimide, a liquid which boils at 76·5°, changes slowly, without external stimulus, into a crystalline, isomeric, diazoamino-compound, which melts at 192° and is very sensitive towards acids. Reflecting on the probable constitution of this compound, we were at first disposed to regard it as having a cycloid structure arising from allylazoimide by the following rearrangement:

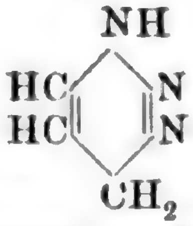


$$CH_2{:}CH{\cdot}CH_2{\cdot}N{<}\begin{smallmatrix}N\\ \|\\ N\end{smallmatrix} \longrightarrow \begin{matrix}CH{:}CH{\cdot}CH_2\\ NH{-}N{:}N\end{matrix}.$$

Such a ring would be called dihydrotriazine, and represents, so far as we have been able to ascertain, a new type of cycloid; it is, in fact, a dihydrobenzene in which one-half of the molecule is replaced by the diazoamino(triazene)-group:

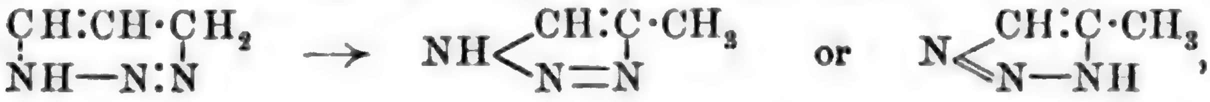


$\Delta^{2:5}$-Dihydrobenzene.



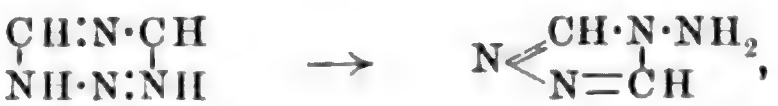
Δ^{5}-Dihydro-1 : 2 : 3-triazine.

In drawing this conclusion, we have not overlooked the possibility of secondary transformation into the isomeric methyl-1 : 2 : 3-triazole,



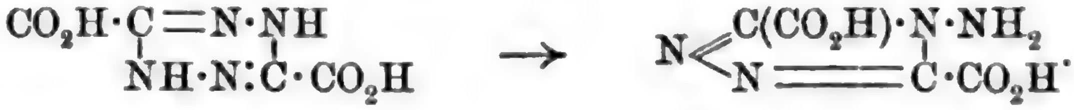
$$\begin{matrix}CH{:}CH{\cdot}CH_2\\ NH{-}N{:}N\end{matrix} \longrightarrow NH{<}\begin{matrix}CH{:}C{\cdot}CH_3\\ N{=}N\end{matrix} \quad\text{or}\quad N{<}\begin{matrix}CH{:}C{\cdot}CH_3\\ N{-}NH\end{matrix},$$

suggested by the recognition of the substance originally called dihydrotetrazine as 1-amino-3 : 4-triazole (Bülow, *Ber.*, 1906, **39**, 2618),



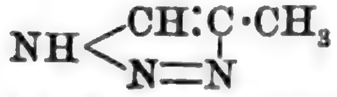
$$\begin{matrix}CH{:}N{\cdot}CH\\ NH{\cdot}N{:}NH\end{matrix} \longrightarrow N{<}\begin{matrix}CH{\cdot}N{\cdot}NH_2\\ N{=}CH\end{matrix},$$

and of *N*-dihydrotetrazinedicarboxylic acid (bisdiazoacetic acid) as 1-amino-3 : 4-triazole-2 : 5-dicarboxylic acid,

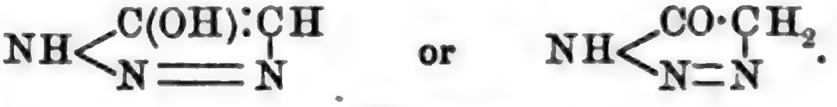


$$\begin{array}{l} CO_2H\cdot C{=}N\cdot NH \\ \qquad\quad NH\cdot N{:}C\cdot CO_2H \end{array} \rightarrow N{<}\begin{array}{l} C(CO_2H)\cdot N\cdot NH_2 \\ N{=\!=\!=}C\cdot CO_2H \end{array}.$$

Our reason for preferring the hexacycloid representation is two-fold. Although the uncertainty hitherto prevailing as regards the constitution of bisdiazoacetic derivatives has been removed by the practical agreement with Bülow's views on the part of Curtius, Darapsky, and Müller (*Ber.*, 1907, **40**, 1470), all doubt as to the possibility of a tetrazine ring existing has been removed since the recent isolation of 1 : 2 : 4 : 5-tetrazine by the authors mentioned (*ibid.*, p. 84). In the second place, if the crystalline isomeride of allylazoimide were 4-methyl-1 : 2 : 3-triazole, it might be expected to resemble the triazolone described by Curtius and Thompson (*Ber.*, 1906, **39**, 4140) as arising from diazoacetamide by the action of baryta :



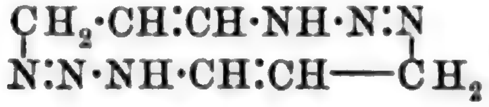
4-Methyl-1 : 2 : 3-triazole.



5-Triazolone.

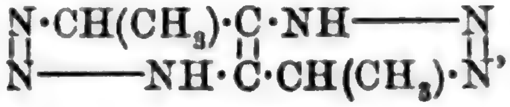
Nevertheless, the two substances are distinguished sharply by their behaviour towards very dilute acids, which forthwith liberate two-thirds of the nitrogen from the compound under discussion, therein recalling the most conspicuous property of the aliphatic diazoamino-derivatives.

It has been mentioned that the transformed allylazoimide melts at 192°, a temperature which suggested a condition of polymerisation, and the elevation of boiling point in chloroform agrees with the formula $(C_3H_5N_3)_2$. This observation might perhaps invite consideration of such complex expressions as



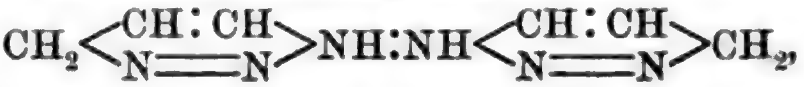
$$\begin{array}{l} CH_2\cdot CH{:}CH\cdot NH\cdot N{:}N \\ N{:}N\cdot NH\cdot CH{:}CH\text{---}CH_2 \end{array}$$

and

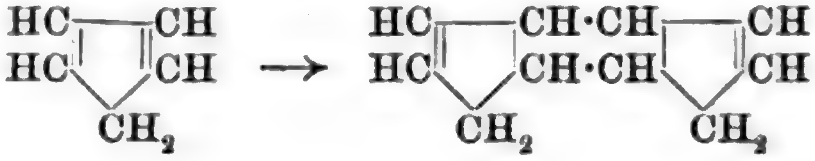


$$\begin{array}{l} N\cdot CH(CH_3)\cdot C\cdot NH\text{------}N \\ N\text{------}NH\cdot C\cdot CH(CH_3)\cdot N \end{array},$$

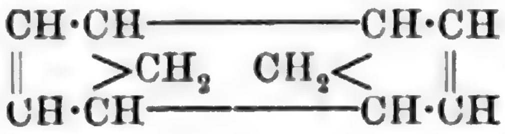
or the possibility of polymerisation being due to change in valency on the part of nitrogen, developing the structure



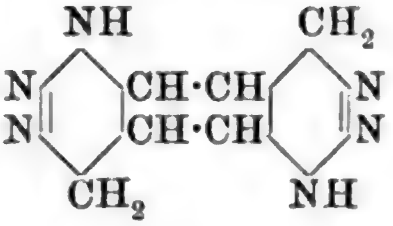
but it seems to us more probable that the case under consideration is allied to that of *cyclo*pentadiene, which has been shown by Krämer and Spilker (*Ber.*, 1896, **29**, 552) to undergo polymerisation with great facility, a change which they represent as follows :



Having in mind Thiele's theory of partial valency, and its application to *cyclo*pentadiene, the alternative:



naturally suggests itself for the polymerised hydrocarbon, but the necessity of maintaining the diazoamino-structure in the transformed allylazoimide leads us to prefer the expression



for that substance.

EXPERIMENTAL.

Allylazoimide, $CH_2{:}CH{\cdot}CH_2{\cdot}N_3$.

The interaction of sodium azide and allyl chloride or iodide was followed under various conditions in the hope of improving the unremunerative yields given by the earlier experiments, but we have had to content ourselves with interrupting the process at a point when the mixture of allylazoimide, its degradation products, and unchanged allyl haloid contains the maximum of triazo-hydrocarbon, which never exceeded 30 per cent. Allyl chloride is more profitable than the iodide, not only on account of initial cost, but also because the boiling point is below that of allylazoimide.

Fifty grams of allyl chloride and 100 c.c. of alcohol were heated under reflux on the water-bath with 50 grams of sodium azide in 150 c.c. of water during two hours, when nitrogen began to escape in small quantities from the faintly yellow liquid, through which a rapid current of steam was then passed; the distillate, diluted with much water, was extracted twice with ether, and the solvent, having been washed with dilute sulphuric acid to remove the basic products of transformation, was shaken several times with water and dried with calcium chloride. On fractionating with a long column of the rod-and-disk pattern, the temperature rose gradually to 76°, and the fraction passing over at 50—76° gave, when twice distilled, a material which boiled steadily at 76·5° under 760 mm. pressure. Using the foregoing quantities, the yield amounted to 15 grams, but was greatly reduced by further distillation, each repetition diminishing the quantity of allylazoimide by about 15 per cent., owing to transformation into the isomeride and its products of change. Although seemingly an individual and free from chlorine, the analysis, for which we are indebted to Mr. Richmond, gave results several per cent. too low, and this must be attributed to loss of nitrogen in the form of hydrazoic acid:

0·1544 gave 40·9 c.c. N_2 at 20·5° and 751 mm., along with 0·02371 of ammonia. N = 30·4 as gas, 15·4 as NH_3; total, 45·8.

$C_3H_5N_3$ requires N = 50·6 per cent.

Allylazoimide is a mobile, refractive liquid, having specific gravity 0·924 compared with water at 25°. The odour is allylaceous, but is less powerful and much sweeter than that of allyl chloride, more closely resembling that of chloroform, whilst the vapour, when inhaled, produces the characteristic throbbing sensation at the base of the forehead. Concentrated sulphuric acid decomposes the azide with vigour, but potash does not liberate gas, although stannous chloride sets free nitrogen immediately; the vapour of allylazoimide explodes when heated, but the detonation is mild.

αβ-Dibromo-γ-triazopropane, $CH_2Br{\cdot}CHBr{\cdot}CH_2{\cdot}N_3$.

On adding a solution of bromine in chloroform to a mixture of allylazoimide with the solvent, the calculated amount of halogen was decolorised without liberation of hydrogen bromide; after fifteen minutes at zero, the liquid was washed with sodium carbonate and distilled in steam, which separated the chloroform from the dibromide. The latter was distilled twice under 5 mm. pressure, boiling steadily at 87°:

0·3442 gave 29·55 c.c. N_2 at 18·7° and 754 mm., along with 0·01937 of ammonia. N = 9·95 as gas, 5·62 as NH_3; total 15·57.

$C_3H_5N_3Br_2$ requires N = 17·28 per cent.

Mr. Richmond, to whom we owe the analysis, reported difficulty in measuring the gas, on account of the mercurous bromide produced, and it is probable that a certain proportion of the nitrogen is lost in this way.

The Diazoamino-compound, $(C_3H_5N_3)_2$, *from Allylazoimide.*

Although a freshly-distilled specimen of allylazoimide undergoes no change with dilute acids, the substance acquires in the course of a few hours the property of effervescing when mixed even with acetic acid. The change on which this alteration of character depends is accelerated by warming the substance to about 50°, and after one or more days, according to circumstances, the liquid deposits large, lustrous, transparent crystals. Recrystallisation from benzene was first attempted, one gram requiring about 400 c.c. of the boiling solvent, but loss of material occurred, and the crystals deposited on cooling, although colourless, were found to retain a basic odour; purification was effected by dissolving one gram in 30 c.c. of boiling chloroform to which 60 c.c. of petroleum (b. p. 60—80°) were then added. Snow-white, odourless plates were thus obtained, melting sharply and decomposing at 192°:

0·1846 gave 0·2955 CO_2 and 0·1045 H_2O. C = 43·65; H = 6·33.
0·1143 ,, 49·3 c.c. N_2 at 16° and 767 mm. N = 51·42.
$C_3H_5N_3$ requires C = 43·37; H = 6·01; N = 50·62 per cent.

The analyses were somewhat complicated by the systematic appearance of nitrous fumes, but Mr. Richmond has confirmed the nitrogen percentage by his method:

0·0689 gave 20·1 c.c. N_2 at 15·7° and 746 mm., along with 0·01138 of ammonia. N = 33·76 as gas, 16·52 as NH_3; total, 50·28.

The diazoamino-compound dissolves more readily in acetone and in chloroform than in benzene, but it is sparingly soluble in ethyl acetate and insoluble in petroleum. Estimation of molecular weight based on the boiling point of chloroform solutions gave 172 and 170, the formula $(C_3H_5N_3)_2$ requiring 166. Hot alcohol and boiling water decompose the substance slowly, although definite products could not be obtained; the decomposition by dilute acids proceeds in a manner analogous to that in which the aliphatic diazoamino-compounds described by Dimroth are degraded, two-thirds of the nitrogen being set free:

0·1176 gave 34·6 c.c. N_2 at 19° and 748 mm. when treated with 5 per cent. hydrochloric acid. N = 33·85.
$C_3H_5N_3$ requires 2/3N = 33·75 per cent.

Several attempts have been made to isolate from the bright red solution definite products of this change, but the small quantity of material at our disposal has prevented a conclusion from being reached. The liquid reduced cold Fehling's solution and ammoniacal silver oxide immediately, the original compound being indifferent to these agents, but on evaporation the reducing properties disappeared, and the platinichloride prepared from the residue was found to be that of ammonium. As might be expected from these indications of its sensitive character, the product of decomposing the diazoamino-compound with acids did not form a stable salt with platinum tetrachloride, the yellow precipitate from which quickly became dark brown.

The power to combine with phenylcarbimide, usually possessed by diazoamino-compounds of this class, is not displayed by the transformed allylazoimide, which was heated with the agent during twenty-four hours. Furthermore, alcoholic ammoniacal silver oxide did not give an insoluble derivative.

ROYAL COLLEGE OF SCIENCE, LONDON,
SOUTH KENSINGTON, S.W.

CXV.—*Aromatic Arsonic and Arsinic Acids.*

By **Frank Lee Pyman** and **William Colebrook Reynolds.**

For some time past we have been engaged in the preparation of aryl derivatives of arsenic, and, as two recent publications (O. and R. Adler, *Ber.*, 1908, **41**, 931; Benda and Kahn, *Ber.*, 1908, **41**, 1672) show that there are other chemists covering somewhat the same ground, we have deemed it advisable to publish our results so far as they have proceeded.

We had prepared 2-aminotolyl-5-arsonic acid and its acetyl derivative some months ago, and these substances together with sodium *p*-aminophenylarsonate have been tested physiologically and clinically. Ehrlich had shown that the toxicity of sodium *p*-acetylaminophenylarsonate is considerably less than that of sodium *p*-aminophenylarsonate, and the same relationship has now been found between the corresponding toluidine derivatives; sodium 2-aminotolyl-5-arsonate has about the same toxicity as sodium *p*-aminophenylarsonate, whilst that of sodium 2-acetylaminotolyl-5-arsonate is very considerably less. These substances have been specially intended for use in trypanosomiasis (sleeping sickness), and experiments on their effect on different strains of trypanosomes have shown that, whilst certain strains were destroyed by the treatment, others were more resistant. In the treatment of syphilis, however, these substances have proved especially efficacious, and the results obtained in this connexion are exceedingly promising. Since O. and R. Adler and Benda and Kahn (*loc. cit.*) have already published the method of preparation and physical properties of these substances, we need only state that we confirm their results, and supplement them by recording the state of hydration of the sodium salts, this latter being important from the point of view of their use in medicine.

In the preparation of *p*-aminophenylarsonic acid and 2-aminotolyl-5-arsonic acid, we have obtained as by-products the corresponding bisaminoarylarsinic acids, which have been briefly alluded to by Benda and Kahn (*loc. cit.*), but, as these have been in our hands for some time past, we give in this communication a full description of their preparation and properties. The constitution of these substances has been proved by replacing the arsenic acid residue by iodine according to the method used by Ehrlich and Bertheim (*Ber.*, 1907, **40**, 3292) for *p*-aminophenylarsonic acid.

The arsinic acids are now being investigated clinically with a view to their possible use in trypanosomiasis and syphilis, but the results are as yet not sufficiently conclusive.

EXPERIMENTAL.

2-Aminotolyl-5-arsonic acid is stated by Benda and Kahn (*loc. cit.*) to melt at 195°; we have found the melting point 198—200°. The constitution of this acid was readily shown by boiling it with dilute sulphuric acid and potassium iodide, when a good yield of 5-iodo-*o*-toluidine melting at 80—85° was obtained. After recrystallisation, this iodo-compound melted at 85° and its acetyl derivative at 168°, and both substances melted at the same temperatures when mixed with the pure substances prepared from aceto-*o*-toluidide.

Sodium 2-aminotolyl-5-arsonate is obtained in glistening, tabular crystals containing three and a-half molecular proportions of water of crystallisation by mixing a highly concentrated aqueous solution with three times its volume of alcohol. When crystallised from water, however, it separates with five molecules of water of crystallisation:

0·4540 air-dried salt (from alcohol) lost 0·0890 H_2O at 130°. $H_2O = 19·6$.

$C_7H_9O_3NAsNa, 3\frac{1}{2}H_2O$ requires $H_2O = 19·9$ per cent.

0·4217 air-dried salt (from water) lost 0·1129 H_2O at 130°. $H_2O = 26·8$

$C_7H_9O_3NAsNa,5H_2O$ requires $H_2O = 26·2$ per cent.

Sodium 2-acetylaminotolyl-5-arsonate separates from 50 per cent. aqueous alcohol in glistening, tabular crystals, which contain five molecules of water of crystallisation. It crystallises from water, however, with seven molecules of water of crystallisation:

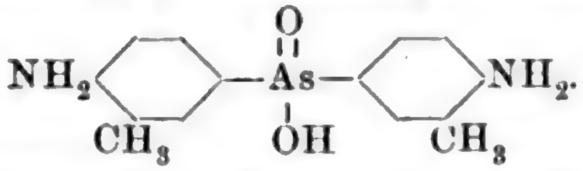
0·4774 air-dried salt (from alcohol) lost 0·1102 H_2O at 100°. $H_2O = 23·1$.

$C_9H_{11}O_4NAsNa,5H_2O$ requires $H_2O = 23·4$ per cent.

0·5210 air-dried salt (from water) lost 0·1560 H_2O at 100° $H_2O = 29·9$.

$C_9H_{11}O_4NAsNa,7H_2O$ requires $H_2O = 29·9$ per cent.

Preparation of Bis-2-aminotolyl-5-arsinic Acid,



Two hundred grams of air-dried *o*-toluidine arsenate and 400 grams of *o*-toluidine were heated over a free flame with constant shaking until the mixture became fluid, and then gently boiled under a reflux condenser for one hour, the heat being regulated so that a thermometer immersed in the liquid registered 180—185°. The mixture was allowed to cool, and extracted with a 10 per cent. solution of sodium carbonate as long as effervescence occurred. The aqueous solution was then evaporated until crystallisation commenced, and allowed to cool. The first crop of sodium 2-aminotolyl-5-arsonate was then separated, well washed with alcohol, and set aside; the mother liquor and alcoholic washings were combined and evaporated to a thick syrup, and this was mixed with several times its volume of alcohol. A second crop of sodium 2-aminotolyl-5-arsonate was thus precipitated, and this was also separated, washed with alcohol, and set aside. The final mother liquors, together with the alcoholic washings, on evaporation to remove the alcohol and subsequent precipitation by hydrochloric acid gave 15 grams of a purple tar; this was dissolved in aqueous sodium hydroxide, evaporated to a small bulk, and allowed to cool, when a quantity of large, prismatic needles separated from the deep-red liquor. These were purified by several crystallisations from water, and proved to be *sodium bis*-2-*aminotolyl*-5-*arsinate*. The quantity of salt actually isolated in a pure state amounted to 6 grams, which represents 3 per cent. of the theoretical, but a considerable quantity, possibly as much again, remained in the deep-red, syrupy mother liquors.

Bis-2-*aminotolyl*-5-*arsinic acid* is obtained by adding the calculated quantity of a mineral acid to the solution of its sodium salt. On crystallisation from boiling water, it forms highly refracting, pointed, microscopic needles, which melt and decompose at 247—249°. It is practically insoluble in cold water and the usual organic solvents, but fairly easily soluble in glacial acetic acid. It is readily soluble in dilute alkalis or mineral acids:

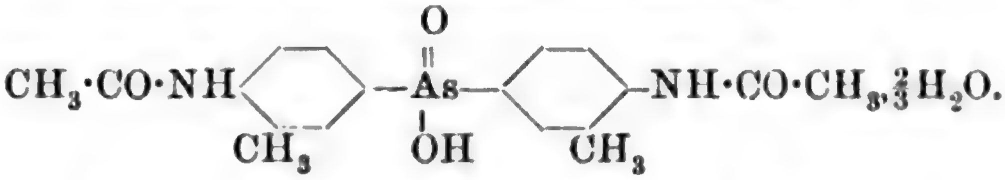
0·1724 gave 0·3332 CO_2 and 0·0840 H_2O. C = 52·7; H = 5·5.
0·0726 „ 5·5 c.c. N_2 at 21° and 763 mm. N = 8·7.
$C_{14}H_{17}O_2N_2As$ requires C = 52·5; H = 5·4; N = 8·7 per cent.

The acid gave a good yield of 5-iodo-*o*-toluidine (m. p. 80—85°) when boiled with dilute sulphuric acid and potassium iodide. After recrystallisation, this iodo-compound melted at 85° and its acetyl derivative at 168°, and both substances melted at the same temperatures when mixed with the pure substances prepared from aceto-*o*-toluidide.

The *sodium* salt, which separates from its aqueous solution in large, hard, prismatic needles, melts in its water of crystallisation at 74—75°, and on further heating loses water, re-solidifies, and does not then melt at 250°. It dissolves in one and a-half times its weight of water at 16°, giving an alkaline solution, and is very easily soluble in alcohol. It contains seven and a-half molecular proportions of water of crystallisation, of which five are lost at 100° and the remainder at 130°:

0·3878 air-dried salt lost 0·0718 H_2O at 100°. $H_2O = 18·5$.
0·3878 „ „ „ 0·1098 H_2O „ 130°. $H_2O = 28·3$.
$C_{14}H_{16}O_2N_2AsNa,7\frac{1}{2}H_2O$ losing $5H_2O$ requires $H_2O = 18·9$ per cent.
$C_{14}H_{16}O_2N_2AsNa,7\frac{1}{2}H_2O$ „ $7\frac{1}{2}H_2O$ „ $H_2O = 28·3$ „

Bis-2-acetylaminotolyl-5-arsinic Acid,



Twenty grams of bis-2-aminotolyl-5-arsinic acid were mixed with 60 grams of acetic anhydride and allowed to stand. After a few minutes, a violent reaction took place, resulting in a clear solution. The liquid was poured into 250 c.c. of water, and, on scratching, 12 grams of white crystals separated. A second crop of 6 grams was obtained by evaporation of the mother liquor; the total yield, 18 grams, represents 71 per cent. of the theoretical.

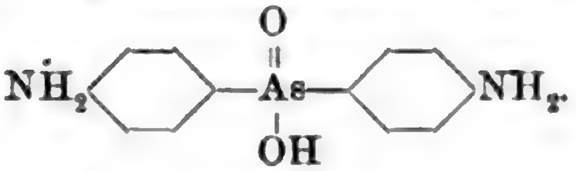
Bis-2-acetylaminotolyl-5-arsinic acid crystallises from boiling water in highly refracting, microscopic prisms and melts at 242—244°. It is practically insoluble in cold water and the usual organic solvents, but fairly easily soluble in glacial acetic acid. It is readily soluble in dilute alkalis, but is insoluble in dilute acids. The acid separates from aqueous solutions with two-thirds of a molecular proportion of water of crystallisation:

0·1656 air-dried salt gave 0·3148 CO_2 and 0·0772 H_2O. $C = 51·8$; $H = 5·2$.
0·4180 air-dried salt lost 0·0124 H_2O at 150°. $H_2O = 3·0$.
0·1898 dried at 150° gave 0·3698 CO_2 and 0·0908 H_2O. $C = 53·1$; $H = 5·4$.
$C_{18}H_{21}O_4N_2As,\frac{2}{3}H_2O$ requires $C = 51·9$; $H = 5·4$; $H_2O = 2·9$ per cent.
$C_{18}H_{21}O_4N_2As$ requires $C = 53·4$; $H = 5·2$ per cent.

The *sodium* salt crystallises from water in radial clusters of silky needles; it melts in its water of crystallisation at 106—107, and on further heating resolidifies and does not then melt at 250°. It dissolves in twice its weight of water at 16°, giving an alkaline solution, and is very easily soluble in alcohol. It contains six molecules of water of crystallisation:

0·1943 air-dried salt lost 0·0393 H_2O at 150°. $H_2O = 20·2$.
$C_{18}H_{20}O_4N_2AsNa,6H_2O$ requires $H_2O = 20·2$ per cent.

Bis-p-*aminophenylarsinic acid*,



This acid results as a by-product in the preparation of *p*-aminophenylarsonic acid by Bechamp's method (*Compt. rend.*, 1863, **56**, 1173). It is most readily isolated in the following manner. The product obtained by heating aniline arsenate with excess of aniline at 180° is extracted with 10 per cent. sodium carbonate solution, the aqueous solution concentrated, and completely precipitated by hydrochloric acid. The precipitate is then digested with just sufficient aqueous sodium hydroxide to give a faintly alkaline solution and filtered from the undissolved matter, which consists of the crude arsinic acid. The latter is then converted into the barium salt, and this is crystallised several times from water, using animal charcoal, until colourless. The pure barium salt is dissolved in water and mixed with the calculated quantity of hydrochloric acid, when the arsinic acid is obtained as a dense, white precipitate of matted needles. The yield amounts to about 2—3 per cent. of the theoretical.

Bis-p-*aminophenylarsinic acid* melts and decomposes at 248—249°. It is very sparingly soluble in water and the usual organic solvents, moderately so in glacial acetic acid, and readily so in dilute alkalis and acids:

0·1358 gave 0·2440 CO_2 and 0·0534 H_2O. $C = 49·0$; $H = 4·4$.
$C_{12}H_{13}O_2N_2As$ requires $C = 49·3$; $H = 4·5$ per cent.

The acid gave a good yield of *p*-iodoaniline (m. p. 62—63°) when boiled with sulphuric acid and potassium iodide.

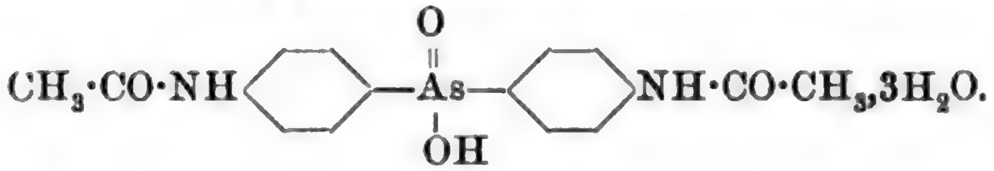
The *sodium* salt crystallises from water in large, monoclinic plates, and melts in its water of crystallisation at 83°, after sintering from 75° onwards. On further heating, it loses water, resolidifies, and does not then melt at 250°; it is soluble in an equal weight of water, giving an alkaline solution, and is very soluble in alcohol. It contains a slightly variable amount of water of crystallisation, the figures obtained on analysis lying between those required for five and six molecular proportions:

0·3979 air-dried salt lost 0·0928 H_2O at 120°. $H_2O = 23·3$.
0·2450 „ „ „ 0·0591 H_2O „ 120°. $H_2O = 24·1$.
0·2492 „ „ „ 0·0616 H_2O „ 120°. $H_2O = 24·7$.
$C_{12}H_{12}O_2N_2AsNa,5H_2O$ requires $H_2O = 22·3$ per cent.
$C_{12}H_{12}O_2N_2AsNa,6H_2O$ „ $H_2O = 25·6$ „

The *barium* salt, which crystallises from water in large, hard prisms, contains seven and a-half molecular proportions of water of crystallisation; it is soluble in twice its weight of cold water, giving an alkaline solution, and is sparingly soluble in alcohol:

0·2562 air-dried salt lost 0·0404 H_2O at 180°. $H_2O = 15·8$.
$(C_{12}H_{12}O_2N_2As)_2Ba,7\frac{1}{2}H_2O$ requires $H_2O = 15·8$ per cent.

Bis-p-*acetylaminophenylarsinic Acid*,



This acid is obtained in an almost quantitative yield by the action of acetic anhydride on bis-*p*-aminophenylarsinic acid. It crystallises from water in rosettes of needles, and melts at 275°. It is very sparingly soluble in the usual organic solvents or cold water, readily so in boiling water, and moderately so in glacial acetic acid. It separates from aqueous solution with three molecules of water of crystallisation:

0·2532 air-dried salt lost 0·0312 H_2O at 120°. $H_2O = 12·3$.
0·1860 dried at 120° gave 0·3484 CO_2 and 0·0740 H_2O. $C = 51·1$; $H = 4·5$.
$C_{16}H_{17}O_4N_2As,3H_2O$ requires $H_2O = 12·6$ per cent.
$C_{16}H_{17}O_4N_2As$ requires $C = 51·1$; $H = 4·6$,,

The *sodium* salt, which separates from water in prismatic needles, melts at about 50° in its water of crystallisation, and on further heating loses water, resolidifies, and does not then melt at 250°. It is soluble in an equal weight of cold water, giving an alkaline solution, and is readily soluble in alcohol. It contains nine molecules of water of crystallisation:

0·3112 air-dried salt lost 0·0908 H_2O at 140°. $H_2O = 29·2$.
$C_{16}H_{16}O_4N_2AsNa,9H_2O$ requires $H_2O = 28·9$ per cent.

THE WELLCOME CHEMICAL WORKS,
DARTFORD, KENT.

CXVI.—*The Electrolytic Oxidation of Some Hydroxybenzoic Acids.*

By Arthur George Perkin and Frederick Mollwo Perkin.

It has been previously shown that when gallic acid (Trans., 1903, **83**, 199) is oxidised by means of potassium ferricyanide in presence of sodium acetate, a compound is formed which, judging from its analogy to purpurogallin, is probably purpurogallincarboxylic acid. Unfortunately, the amount of product so obtained was far too meagre to admit of any extended investigation, but, as it was subsequently ascertained that purpurogallin itself can be very conveniently prepared by the electrolytic oxidation of pyrogallol under certain circumstances (Trans., 1904, **85**, 243), a study of the behaviour of gallic acid in this respect was also instituted. As a result, considerably larger yields of purpurogallincarboxylic acid were obtained, and by a further investigation of the process a still greater improvement in this respect has been effected. The main results of this work have been completed for some time, but their communication has been delayed in the hope that the constitution of purpurogallin itself would have been elucidated. An important point in this respect has been the fact that the first product of the oxidation is probably the compound $C_6H_4O_3$ (Trans., 1906, **89**, 803), which appears to be a hydroxy-*o*-benzoquinone and is obtained by the action of amyl nitrite on an alcoholic solution of pyrogallol, for this in boiling aqueous solution is partly converted into purpurogallin. A preliminary account of the further study of the colouring matter itself has been given (Proc., 1905, **21**, 212), but the continuation of the investigation was postponed until other work of a more pressing character had been completed. The investigation has now been undertaken afresh, but, as some time may elapse before results of special interest accumulate, it seemed advisable to communicate to the Society the points enumerated in the following pages.

Electrolytic Oxidation of Gallic Acid.

1. *Electrolyte*:—*Sodium Sulphate.*

The first experiments were made under practically similar conditions to those which had given the most satisfactory results in the electrolytic oxidation of pyrogallol. The gallic acid was dissolved in a 15 per cent. solution of sodium sulphate slightly acidified with sulphuric acid, but, owing to its sparing solubility, only comparatively dilute solutions could be used. Twenty grams of gallic acid were dissolved in 1 litre of 15 per cent. sodium sulphate solution, and then 5 c.c. of $4N$-sulphuric acid were added. In order to obtain solution, it was found necessary to grind up the gallic acid into a thin cream with water, and to add this to the sodium sulphate solution. The mixture was then agitated by means of a glass stirrer until the gallic acid had completely dissolved, the sulphuric acid was then added, and the solution electrolysed. As anodes two pieces of sheet platinum having each a surface of 750 sq. cm. were used, the total anode surface being therefore 1·5 sq. dcm. The cathode consisted of a lead paddle with a surface of 0·5 sq. dcm., which during the electrolysis was rotated by means of a small electromotor. It should be mentioned here that preliminary experiments had shown that the best results were obtained when the anode and cathode compartment were not separated. In order to prevent rise of temperature, the electrolysing vessel was placed in an outer vessel through which cold water was circulated. A current of 4 amperes was passed for seven hours, the E.M.F. being 7 volts. When the action commenced, the solution became yellow, but this gradually darkened, and at the end of fifteen minutes an almost black liquid had been produced.

After the electrolysis was finished, the mixture was allowed to stand overnight, when a fine black precipitate had settled to the bottom of the vessel. The precipitate was collected, repeatedly washed with cold water until the wash-water was colourless, and drained on a porous tile. The average yield of the product was 34 per cent. of the gallic acid employed. This method of procedure gives the free acid. It was afterwards found, however, that better results were obtained when sodium acetate was employed, the sparingly soluble sodium salt of the acid being thus produced. Experiments were also tried with potassium, calcium, ammonium, and magnesium acetates, but the yields were in no case so good as when sodium acetate was employed, and the product was not so pure.

2. *Electrolyte:—Sodium Acetate.*

Thirty grams of gallic acid were ground into a paste with a 15 per cent. solution of sodium acetate. The paste was then poured into 800 c.c. of the same solution, well stirred, and the clear liquid electrolysed with the same electrodes as those mentioned above. The solution became yellow on the passage of the current, but gradually darkened, and finally assumed a brownish-black tint. The current employed was 2·5—3 amperes with an E.M.F. of 5—6 volts, and the electrolysis was continued for about eight hours. After standing overnight, the precipitate was collected, washed with cold water, and finally with alcohol. The yield varied between 30 and 40 per cent. of the gallic acid taken.

The product of oxidation consisted of an orange-brown, crystalline powder, which, under the microscope, was seen to consist of thin plates or leaflets, and was evidently a sodium salt. An analysis of the substance, dried at 160°, indicated that it is an almost pure *sodium purpurogallincarboxylate*.

Found : Na = 7·85.

$C_{12}H_7O_7Na$ requires Na = 8·04 per cent.

A determination of the water of crystallisation found to be present in this preparation was made at 160° on a sample which had been dried in the air for several days. The analysis showed it to contain $4H_2O$:

Found : $H_2O = 20{\cdot}05$.

$C_{12}H_7O_7Na,4H_2O$ requires $H_2O = 20{\cdot}11$ per cent.

In the anhydrous condition, this substance is hygroscopic, and, on standing overnight, regained one molecule of water :

Found : $H_2O = 5{\cdot}00$.

Theory requires $H_2O = 5{\cdot}92$ per cent.

Sodium purpurogallincarboxylate is sparingly soluble in boiling water, and from a concentrated solution is deposited on cooling in microscopic needles, which contain no water of crystallisation. When digested with a boiling aqueous solution of potassium acetate, the filtered liquid, on cooling, deposits the *potassium* salt in prismatic needles, closely resembling purpurogallin itself. An analysis of this compound, dried at 160°, gave :

Found : K = 12·95.

$C_{12}H_7O_7K$ requires K = 12·91 per cent.

The air-dried substance, heated to 160°, loses three molecules of water of crystallisation :

Found : $H_2O = 15{\cdot}16, 15{\cdot}37$.

$C_{12}H_7O_7K,3H_2O$ requires $H_2O = 15{\cdot}17$ per cent.

A boiling aqueous solution of potassium purpurogallincarboxylate, on cautious treatment with barium chloride, deposits minute, orange-red, prismatic needles, which consist of the corresponding *barium* salt, almost insoluble in water. When dried at 160°, it gave :

Found : Ba = 20·96.

$(C_{12}H_7O_7)_2Ba$ requires Ba = 20·66 per cent.

When these salts are decomposed with boiling dilute hydrochloric acid, *purpurogallincarboxylic acid* is obtained as a semi-gelatinous precipitate, which, after drying, is but sparingly soluble in any of the usual solvents. From nitrobenzene, it is deposited as small, orange-coloured needles, but, as a very large amount of the solvent would be necessary for the preparation of even a gram in this condition, a simpler method of purification was desirable. The difficulty was overcome by employing the crude acid recently precipitated from its sodium salt in the moist condition, as this dissolved somewhat readily in boiling alcohol. On partly evaporating the solution, crystals separated on cooling, which were collected while the mixture was still warm and washed with dilute alcohol. A chemically pure product could thus be usually obtained in one such operation, but, if further purification was necessary, the product was again rendered soluble in alcohol by reprecipitation and crystallised in a similar manner:

Found: $C = 54{\cdot}37$; $H = 3{\cdot}24$.
$C_{12}H_8O_7$ requires $C = 54{\cdot}54$; $H = 3{\cdot}03$ per cent.

Purpurogallincarboxylic acid usually crystallises in minute, orange-yellow leaflets, which are devoid of water of crystallisation, does not melt below 300°, and on strong heating yields a trace of a crystalline sublimate, apparently consisting of the unchanged acid. Occasionally the acid is deposited from dilute alcohol in needles, and it is possible that in this variety, although but rarely obtained, water of crystallisation is present. As previously stated, this compound (Trans., 1903, **83**, 200) gives with alkaline solutions the characteristic colour reactions of purpurogallin itself, and, moreover, possesses strong mordant dyeing properties, which closely resemble those given by the same colouring matter. Further attempts to prepare the acetyl derivative in a pure condition have been unsuccessful, the product hitherto obtained being, curiously enough, too soluble to admit of crystallisation.

It is readily attacked by bromine in the presence of acetic acid or alcohol, but no sparingly soluble derivative of the nature of dibromopurpurogallin is thus formed. Up to the present a definite product of the reaction has not been isolated, but, as apparently in this manner both substitution and decomposition simultaneously occur, the reaction will be studied with a larger quantity of material, when this is available.

Methyl Purpurogallincarboxylate Tetramethyl Ether, $C_{11}H_3O(OMe)_4{\cdot}CO_2Me$.—Purpurogallincarboxylic acid, or the crude sodium salt, electrolytically prepared and suspended in methyl alcohol, was treated with equivalent quantities of methyl sulphate and concentrated potassium hydroxide solution until a final addition of the latter did not produce a change of coloration. The methylation did not proceed readily, a very large excess of the reagents being necessary for its completion, reminding one of the behaviour of alizarin in similar circumstances. The product was poured into ether, the ethereal liquid well washed with dilute alkali, evaporated, and the residue purified by crystallisation from alcohol. The yield was approximately 25 per cent.:

Found: C = 61·08; H = 5·70; CH_3 = 21·91.

$C_{17}H_{18}O_7$ requires C = 61·07; H = 5·39; CH_3 = 22·45 per cent.

It consists of very pale yellow, almost colourless needles, melting at 120—121°, sparingly soluble in alcohol, and resembling purpurogallin tetramethyl ether.

To determine if this compound was an ester, it was digested with boiling dilute alcoholic potash for a few minutes. Addition of water did not cause the separation of a precipitate, and the clear liquid was neutralised with acid. On cooling, fine needles separated, which were collected and recrystallised from dilute alcohol:

Found: C = 59·93; H = 5·12; CH_3 = 18·40.

$C_{16}H_{16}O_7$ requires C = 60·00; H = 5·00; CH_3 = 18·75 per cent.

Purpurogallincarboxylic acid tetramethyl ether, $C_{11}H_3O(OMe)_4{\cdot}CO_2H$, consists of small, faintly-yellow needles, melting at 182—183°, readily soluble in alcohol, and more sparingly so in benzene, from which it crystallises in minute needles.

Purpurogallonecarboxylic Acid, $C_{11}H_7O_5{\cdot}CO_2H$.

It was previously shown by Perkin and Steven (*loc. cit.*) that when purpurogallin is digested with boiling 50 per cent. aqueous potassium hydroxide, it is converted into two isomeric compounds having the same formula as purpurogallin itself, and it was therefore interesting to determine if a similar change occurs when purpurogallincarboxylic acid is so treated. A solution of 3 grams of the acid in 30 c.c. of the potassium hydroxide solution was boiled in an open flask until a test portion on dilution with water did not develop a green tint. The product, when cautiously treated with dilute sulphuric acid, deposited an orange-coloured, sandy precipitate, which on examination under the microscope was seen to consist of fine needles. These were collected, dissolved in boiling alcohol, the solution poured into ether, and, after removal of insoluble matter, the ethereal liquid was well washed with water and evaporated. The concentrated alcoholic solution of the residue at first deposited a trace of unattacked purpurogallincarboxylic acid, which was removed, and the addition of a little boiling water to the filtrate now caused the separation of bright yellow needles. These were further purified by crystallisation from dilute alcohol:

Found: C = 54·81; H = 3·27.

$C_{12}H_8O_7$ requires C = 54·54; H = 3·03 per cent.

As thus prepared, the substance appeared to be homogeneous, and no two distinct forms could be separated, as was previously found to be the case with the product obtained from purpurogallin itself. In the recently precipitated moist condition, *purpurogallonecarboxylic acid* is somewhat readily soluble in boiling alcohol, and on evaporating the solution it separates in the crystalline condition. When fractionally treated in this manner, the first deposit contained but a trace (2·48 per cent.) of water of crystallisation, whereas in the second, approximately two molecules of water of crystallisation were present:

Found: $H_2O = 11·27, 11·15, 11·88$.

$C_{12}H_8O_7,2H_2O$ requires $H_2O = 12·0$ per cent.

Whereas the anhydrous variety is sparingly soluble in hot alcohol the hydrated form readily passes into solution, but, if the latter when concentrated is digested at the boiling point, the solution quickly becomes semi-solid, owing to the separation of the anhydrous substance. Under the microscope both varieties were seen to consist of prismatic needles, and no special difference could be observed between them. Purpurogallonecarboxylic acid does not melt below 300°, and is soluble in alkalis with a yellow colour, which, on exposure to air, becomes deep crimson-red. If air is passed through the alkaline liquid until the latter tint is fully developed, the solution acidified, extracted with ether, and the extract evaporated, an amorphous residue is obtained, which on drying intumesces in the manner characteristic of the tannins. Purpurogallincarboxylic acid, treated in a similar manner, gives an analogous product, but attempts to prepare these compounds in a pure condition have been hitherto unsuccessful. Purpurogallonecarboxylic acid dyes mordanted wool in shades almost identical with those given by the purpurogallones (*loc. cit.*):

Chromium.	Aluminium.	Tin.	Iron.
Chocolate-brown	Pale chocolate-brown	Pale yellow	Chocolate-brown

With alcoholic lead acetate, it gives a yellow precipitate, and with alcoholic ferric chloride a deep brownish-black coloration.

Action of Acetic Anhydride.—The acid (1 gram) is but slowly attacked by boiling acetic anhydride (10 c.c.), but on addition of six drops of pyridine a clear liquid is almost instantaneously produced, and the reaction is complete after a few minutes' digestion.* On pouring into water, an oily product separated, which rapidly became crystalline, and this was collected and, in the earlier experiments, purified by crystallisation from alcohol, in which it is sparingly soluble. Curiously enough, however, much loss occurs during the latter treatment, a yield of only 15 per cent. being thus obtained, but this loss was subsequently avoided by crystallisation from a mixture of benzene and nitrobenzene:

---

* It was noted in previous work with ellagic and flavellagic acids (*loc. cit.*) that, whereas these compounds are but slowly attacked by acetic anhydride when in the dry condition, if pyridine of crystallisation was present the production of their acetyl derivatives was much more rapid. Experiments carried out with numerous other substances indicated that pyridine employed in the above manner greatly facilitates the acetylation process, and in every case was preferable to the employment of sodium acetate. With compounds of the nature of alizarin or quercetin, which yield sparingly soluble acetyl derivatives, and employing the usual quantity of the reagents, only six or ten drops of pyridine for one gram of the phenol are

Found: C = 58·10; H = 3·24.

$C_{12}H_4O_6(C_2H_3O)_2$ requires C = 58·18; H = 3·03 per cent.

During the acetylation therefore of purpurogallonecarboxylic acid, a molecule of water is simultaneously removed, which was also (*loc. cit.*) shown to be the case when purpurogallones themselves were similarly treated. An estimation of the acetyl groups was carried out by the ethyl acetate method (Trans., 1905, **87**, 107):

Found: $C_2H_4O_2$ = 37·81.

Theory requires $C_2H_4O_2$ = 38·21 per cent.

During the hydrolysis, the acetyl compound unites with a molecule of water and is reconverted into purpurogallonecarboxylic acid, which is readily isolated by cautious addition of boiling water to the residual alcoholic liquid. *Acetylanhydropurpurogallonecarboxylic acid* forms colourless needles, melting at 236—238° with effervescence.

It has previously been shown (*loc. cit.*) that when *iso*purpurogallone is dissolved in sulphuric acid, the anhydro-compound, $C_{11}H_6O_4$, is formed, and can be isolated by means of acetic acid. Experiments with the acid in a similar manner gave, however, a yellow product, which consisted of the unaltered compound, as analysis showed:

Found: C = 54·56; H = 3·52 per cent.

Although judging by the results of the acetylation there is every reason to suppose that the acid $C_{11}H_5O_4{\cdot}CO_2H$ is formed by the action of the sulphuric acid, it is evidently of a less stable nature than the corresponding *iso*purpurogallone derivative, $C_{11}H_6O_4$, and readily regenerates the purpurogallonecarboxylic acid during the process employed for its isolation. Such a change evidently takes place, although less readily, when the acetyl derivative is dissolved in alcohol, but this can be avoided, as shown above, by the employment of a solvent in which the absence of water can be ensured.

necessary. The pyridine is added to the boiling mixture, and the reaction is completed by digestion for a few minutes. On treating the product with alcohol, the acetyl compound separates in a crystalline condition, and is frequently thus isolated in a state of chemical purity. In cases where the acetyl compound is of a more soluble nature, precipitation with water and procedure in the usual manner is adopted.

Methyl purpurogallonecarboxylate tetramethyl ether,

$C_{11}H_3O(OMe)_4\cdot CO_2Me$,

can be obtained in an identical manner to that employed for the preparation of the corresponding ether of methyl purpurogallincarboxylate, In this case, also, very large quantities of methyl sulphate and alkali are necessary, and the yield is poor. After removal of products soluble in alkali, the residue consisted principally of the anticipated compound, but a trace of a second methyl ether, too small in quantity for characterisation, was also present. By extraction with light petroleum, the latter remained undissolved, and, on concentrating the extract and cooling, colourless prisms separated, which melted at 110—111°:

Found: $C = 61.27$; $H = 5.55$; $CH_3 = 21.69$.

$C_{17}H_{18}O_7$ requires $C = 61.08$; $H = 5.39$; $CH_3 = 22.45$ per cent.

It was noted that the hydriodic acid liquid from the Zeisel determination contained crystals of purpurogallonecarboxylic acid.

Purpurogallonecarboxylic acid tetramethyl ether, $C_{11}H_3O(OMe)_4\cdot CO_2H$, is produced, as might be anticipated, by a short digestion of the ester compound with alcoholic potash. On addition of water, the liquid remained clear, and when this was neutralised with acid an oil separated which rapidly became solid. It was purified by crystallisation from benzene, from which it is deposited as small, colourless needles:

Found: $C = 60.13$; $H = 5.15$.

$C_{16}H_{16}O_7$ requires $C = 60.00$; $H = 5.00$ per cent.

From alcohol, in which it is readily soluble, it crystallises in colourless prisms. It melts at 166—167°, and on treatment with hydriodic acid is converted into purpurogallonecarboxylic acid. By prolonged digestion with boiling alcoholic potash, this tetramethyl ether is not further attacked, and it thus appears evident that only one carboxyl group is present in this compound. The suggestion which was made in the earlier paper (*loc. cit.*) that the formation of the purpurogallones from purpurogallin was probably due in part to the oxidation of an alcoholic to a carboxylic group, cannot thus be considered feasible.

A study of the oxidation products of purpurogallin tetramethyl ether and of the corresponding derivative of purpurogallincarboxylic acid will be shortly undertaken, as it is hoped that the constitution of these interesting compounds will thus be elucidated.

The Electrolytic Oxidation of Gallic and Protocatechuic Acids in the Presence of Sulphuric Acid.

It has been previously shown (Trans., 1905, **87**, 1412; 1906, **89**, 251) that when gallic acid is oxidised with potassium persulphate in the presence of sulphuric acid, it is converted into ellagic acid and flavellagic acid (hydroxyellagic acid). On the other hand, when 60 per cent. sulphuric acid is employed, flavellagic acid is alone produced, and, again, if a mixture of acetic and sulphuric acids forms the solvent, ellagic acid alone is obtained. With the simpler hydroxybenzoic acids, similarly constituted compounds, but containing fewer hydroxyl groups, are produced, whereas the highest member of the series, dihydroxyellagic acid, is formed by heating ellagic acid with sulphuric acid to a high temperature. It appeared interesting to study the electrolytic oxidation of these acids in case any new points of interest might be revealed, although it seemed probable from a somewhat early patent dealing with this subject, which, however, we did not see until the work was nearly completed (Badische Anilin- und Soda-Fabrik, D.R.-P. 85390), that the reaction was likely to follow the same lines as when persulphate was employed.

Gallic Acid.

The solution employed in these experiments was prepared by first stirring finely-powdered gallic acid (20 grams) with sulphuric acid until a thin cream was produced, and subsequently diluting with the acid until the volume of the mixture was about 90 c.c. From 10 to 15 c.c. of water were added, and the whole was then warmed until a clear liquid was obtained. Preliminary experiments carried out without a separation of the anode and cathode compartments gave an indifferent yield of the oxidation product, and the effect was now studied of separating the anode and cathode by means of a porous cell. A small beaker was therefore employed for the anode solution, and the cathode solution was contained in a porous cell, which was placed in the centre of the beaker, rise of temperature being avoided by standing the arrangement in a basin through which cold water was circulated. As the results, however, were still disappointing, the sheet anode was removed, and one consisting of coiled platinum wire having a total active surface of 5 sq. cm. was substituted, and by this means a very much better yield of the oxidation product was obtained. In the first experiments, the anode current density was 4 amperes per sq. dcm., the E.M.F. being 4·5—5·3 volts, whereas in the latter it was 40 amperes per sq. dcm. and the E.M.F. 6—7 volts. Care was taken not to allow the temperature to rise above 20°. As the best results were obtained with a high current density, and, as with the concentration of the sulphuric acid used this would represent favourable conditions for the formation of persulphuric acid, it is probable that the oxidation is not directly electrolytic, but is due to the action of the persulphuric acid first produced.

According to the equation

$$2C_7H_6O_5 = C_{14}H_6O_9 + 3H_2O,$$

20 grams of gallic acid would require the passage of six ampere-hours, but it was found more advantageous to pass the current for eight ampere-hours. The product was heated to 50° for one hour, poured into a large excess of water, and the precipitate collected and well washed. The average yield was 20 per cent., but occasionally as much as 30 per cent. of the substance was obtained.

Subsequently, a third method was employed, which gave a still better result. In this case the anode consisted of a platinum U-tube with a diameter of 0·33 cm. and having a total active surface of 9 sq. cm., and this was placed in the porous cell which now constituted the anode compartment. During the electrolysis, water was passed through the tube, so that, not only the solution, but the electrode itself was thus kept cold. The cathode consisted of a platinum wire which surrounded the anode cell, and with a current of 2 amperes the E.M.F. varied between 7 and 8 volts, the current density being therefore 0·22 ampere per sq. cm. By this method, it was possible to obtain a yield of 40 per cent. of the oxidation product, although owing to the small size of the platinum tube employed it was not possible to work with large quantities of material.

The product of the reaction consisted of a greenish-yellow powder of an apparently pure character, very sparingly soluble in the usual solvents, and readily soluble in alkalis with a well-marked green tint. It was evidently not identical with the compound described in the patent of the Badische Anilin- und Soda-Fabrik (*loc. cit.*), as prepared by the oxidation of gallic acid in the presence of sulphuric acid, for the latter has the property of giving a blue coloration with sodium carbonate solution.

For purification, crystallisation from pyridine was resorted to, a very large quantity of the solvent being necessary. The solution, on cooling, deposited a voluminous mass of small, yellow needles containing pyridine of crystallisation. These were collected, washed with pyridine, and finally with alcohol, by which latter treatment the crystals shrunk to a very small bulk. The product was dried at 160°:

Found: C = 52·80; H = 2·12.

$C_{14}H_6O_9$ requires C = 52·83; H = 1·89 per cent.

It did not melt below 360°, gave with nitric acid the Griesmayer reaction, and evidently consisted of flavellagic acid. To prepare the acetyl derivative, the finely-powdered substance suspended in much boiling acetic anhydride was treated with a few drops of sulphuric acid, and the mixture digested at the boiling point for fifteen minutes. The clear liquid, on boiling, became semi-solid, owing to the separation of long, hair-like, colourless needles, which were collected and recrystallised from acetic anhydride:

Found: C = 54·59; H = 3·51.

$C_{14}HO_9(C_2H_3O)_5$ requires C = 54·54; N = 3·03 per cent.

It melted at 317—319°, and consisted without doubt of acetylflavellagic acid.

It is consequently evident that when a solution of gallic acid in 60 per cent. sulphuric acid is oxidised either electrolytically or by means of persulphates, the same compound, namely, flavellagic acid, is produced.

Protocatechuic Acid.

The method of procedure in this case was similar to that employed for the oxidation of gallic acid. The protocatechuic acid was dissolved in concentrated sulphuric acid, and the solution then diluted by the addition of a small quantity of water. The anode was a spiral of platinum wire having a surface of 5 sq. cm., and a current density of 20 amperes per sq. dcm. was employed. When the electrolysis was complete, the product was heated to 50° for an hour, poured into water, and the precipitate collected and washed; the yield, however, was poor, and in no case was more than 10 per cent. of the oxidation product obtained.

The substance, which consisted of a pale brown, crystalline powder, was evidently of a much purer character than that usually obtained by means of persulphates. On account of its sparing solubility, it was acetylated with a large volume of acetic anhydride to which a small quantity of sulphuric acid had been added. The product was purified by recrystallisation from acetic anhydride;

Found: C = 60·82; H = 3·18.

$C_{14}H_4O_6(C_2H_3O)_2$ requires C = 61·01; H = 2·82 per cent.

It consisted of colourless, prismatic needles melting at 322—324°, and was identified as acetylcatellagic acid. The catellagic acid produced by the hydrolysis of this compound was characterised by the readiness with which it sublimed at high temperatures, and differed in no respect from the compound obtained by the agency of persulphates.

A study of electrolytic oxidation of *p*- and *m*-hydroxybenzoic acids gave somewhat disappointing results, and it soon became evident that the employment of persulphate for the oxidation of these acids in this respect was much more advantageous. The subject has consequently been put on one side, but it is hoped that by employing the water-cooled anode, as in the experiments with gallic acid, a more satisfactory result may be obtained.

THE CLOTHWORKERS' RESEARCH LABORATORY,
THE UNIVERSITY, LEEDS.

BOROUGH POLYTECHNIC INSTITUTE,
LONDON, S.E.

CXVII.—*The Thermal Decomposition of Hydrocarbons. Part I.** [*Methane, Ethane, Ethylene, and Acetylene.*]

By WILLIAM ARTHUR BONE and HUBERT FRANK COWARD.

MUCH has been written concerning the action of heat on hydrocarbons, and the separation of carbon in flames, since Dalton and William Henry conjointly studied the decomposition of methane and ethylene when subjected to the continued action of electric sparks (Dalton's "*New System*," vol. I, pp. 440, 447; *Phil. Trans.*, 1809, **99**, 446). Owing, however, to the complexity of the phenomena, and the difficulty in realising conditions under which crucial evidence can be obtained, we are still far from understanding the precise modes of decomposition of even the simplest hydrocarbons, whilst the final elucidation of the question as it affects the higher members of the various series will probably tax our experimental resources to the utmost for many years to come.

That the ultimate resolution of a hydrocarbon into its elements at high temperatures cannot be regarded in general as the immediate result of a single chemical change was proved by Marchand in 1839 (*J. pr. Chem.*, **36**, 478), when he obtained large quantities of methane during the decomposition of ethylene at a bright red heat. This led him to represent the initial stage of the transaction as involving the simultaneous liberation of carbon and methane as follows:

$$C_2H_4 = C + CH_4.$$

This view derived some support from the later observation of Buff and Hofmann (*Annalen*, 1860, **113**, 129), that when a platinum wire is electrically heated to dull redness in ethylene, the gas is decomposed, yielding carbon and much methane without any appreciable change in volume. But the cogency of this otherwise important piece of evidence is weakened, as V. B. Lewes has justly remarked, by the fact that denser hydrocarbons, both solid and liquid, are undoubtedly formed from ethylene at incipient red heat.

---

* A preliminary notice of this investigation appeared under the names of Bone and Jerdan in the *Proceedings*, 1901, **17**, 164.

During the years 1863—1869, Berthelot made a comprehensive study of the behaviour of hydrocarbons at high temperatures (*Ann. Chim. Phys.*, 1863, [iii], **67**, 53; 1866, [iv], **9**, 413, 455; 1867, [iv], **12**, 5, 122; 1869, [iv], **16**, 143, 148, 153, 162). He contended that a hydrocarbon is never directly resolved into its elements, but the primary change always involves either a polymerisation (for example, acetylene to benzene), or a coalition of two or more molecules to form a denser hydrocarbon with elimination of hydrogen. These denser molecules in turn undergo a series of similar changes until carbon finally appears as the result of the decomposition of an extremely complex molecular aggregation. In elaborating this idea he convinced himself that the successive changes involved in the decomposition of any particular hydrocarbon are usually either all individually reversible or may be so grouped as to comprise a series of reversible cycles, and that therefore at any given temperature there would finally be established a complex state of equilibrium between hydrogen, methane, ethane, ethylene, acetylene, benzene, styrolene, diphenyl, anthracene, naphthalene . . . and carbon.* In no case, however, was the attainment of such a state of equilibrium ever proved by any quantitative measurements; it was considered sufficient to obtain qualitative evidence of the reversibility of the principal individual reactions and to deduce the general theory by the application of first principles.

With regard to the four hydrocarbons dealt with in the present paper, Berthelot maintained that methane is primarily decomposed either into acetylene and hydrogen, or possibly into ethane and hydrogen, in accordance with one or other of the following equations:

$$(a)\ 2CH_4 = C_2H_2 + 3H_2 \qquad (b)\ 2CH_4 = C_2H_6 + H_2.$$

---

* Berthelot's views are summarised in the following passage from one of his memoirs (*Ann. Chim. Phys.*, 1866, [iv], **9**, 471). ". . . . que la décomposition immédiate d'un carbure d'hydrogène ne répond pas à sa résolution en éléments, mais à sa transformation en polymères, ou en carbures plus condensés avec perte d'hydrogène. Cette transformation ne s'effecte point d'ailleurs à une température absolument fixe et comparable à celle d'ébullition d'un liquide; mais elle s'opère pendant un vaste intervalle de température compris entre le rouge sombre et le rouge blanc: durant cet intervalle le carbure est décomposé en proportion d'autant plus forte et avec une vitesse d'autant plus grande que la température est plus élevée. . . . Entre chaque genre de réaction et la réaction réciproque il s'établit fréquemment une sort d'équilibre mobile, variable avec la température et les corps q se trouvent en présence, équilibre analogue à celui qui se produit lors la dissociat des composés binaires."

Ethane, he considered, yields either ethylene and hydrogen, or acetylene, methane, and hydrogen, as follows:

$$(c)\ C_2H_6 = C_2H_4 + H_2 \qquad (d)\ 2C_2H_6 = 2CH_4 + C_2H_2 + H_2,$$

whilst ethylene yields either acetylene and hydrogen, or acetylene and ethane,

$$(e)\ C_2H_4 = C_2H_2 + H_2 \qquad (f)\ 2C_2H_4 = C_2H_6 + C_2H_2.$$

He regarded acetylene as "le produit ultime des décompositions pyrogenées . . . . générateur fondamental des carbures pyrogenées." It exhibits in a high degree the power of polymerising, or of condensing with either hydrogen or aromatic hydrocarbons at high temperatures, but it is never directly resolved into its elements.

But plausible and attractive as Berthelot's theory may appear, evidence of its insufficiency was soon forthcoming. In 1873 T. E. Thorpe and J. Young, as the result of an investigation on the combined action of heat and pressure on the paraffins (*Proc. Roy. Soc.*, **21**, 184), concluded that the primary decomposition gives rise to an olefine and a lower paraffin without loss of hydrogen somewhat as follows:

$$CH_3\cdot CH_2\cdot CH_2\cdot CH_3 = CH_3\cdot CH_3 + CH_2{:}CH_2.$$

Moreover, in 1886, H. E. Armstrong and A. K. Miller (Trans., **49**, 74) drew attention to the almost complete absence of acetylene and its homologues from the products of the manufacture of oil gas from petroleum, which were found to consist largely of ethylenic and benzenoid hydrocarbons, and suggested that the latter may be derived directly from the corresponding paraffins (for example, benzene from hexane) without the intervention of acetylene.

The work of V. B. Lewes, chiefly on ethylene, forms one of the most notable recent contributions to our knowledge of the subject (*Proc. Roy. Soc.*, 1894, **55**, 90; 1895, **57**, 394). He concluded that ethylene is primarily resolved into equal volumes of acetylene and methane as the result of the following termolecular change:

$$(g)\quad 3C_2H_4 = 2C_2H_2 + 2CH_4,$$

and that the acetylene subsequently either polymerises or is resolved into its elements, according to the temperature. With regard to methane, he agreed with Berthelot that it is initially transformed into acetylene and hydrogen in accordance with the equation (*a*).

In 1896 Haber (*Ber.*, **29**, 2691) published a paper on the decomposition of the higher paraffins, in which he vigorously assailed Berthelot's views. In the case of *n*-hexane, he conclusively proved that at temperatures between 600° and 800° the primary decomposition involves the elimination of methane and the simultaneous formation of one of the next lower olefines, C_5H_{10}, in accordance with the equation

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 = CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2 + CH_4,$$

a change which he regarded as typical of all the higher paraffins. In the aromatic series, on the contrary, he recognised a marked disposition to form more complex molecules with the elimination of hydrogen, for example, diphenyl from benzene:

$$2C_6H_6 = C_{12}H_{10} + H_2.$$

Haber's views as to the behaviour of acetylene at high temperatures show how completely he accepted the prevailing notion of its inherent superior stability over that of all other hydrocarbons. He believed that, whilst at 600° it polymerises rapidly and at 800° yields large quantities of hydrogen, it is, nevertheless, at higher temperatures "in starker Verdünnung jedem anderen Kohlenwasserstoff an Beständigkeit überlegen." He severely criticised Lewes' work, however, and rejected the acetylene theory of the luminosity of hydrocarbon flames.

In spite of the counterbalancing weight of evidence derived from the behaviour of the higher paraffins, there has undoubtedly been a tendency during recent years to overestimate the importance of acetylene as a factor in the breaking down of hydrocarbons at high temperatures, as shown in Lewes' attempt to identify the primary formation and subsequent decomposition of acetylene as the sole cause of the luminosity of hydrocarbon flames, a doctrine which has, unfortunately, crept into many reputable text-books. But the experimental evidence on which such views have been based seems to us wholly insufficient and lacking in cogency. The detection of quite insignificant quantities of acetylene among the decomposition products in a particular experiment has far too often been put forward as satisfactory proof of its primary and predominant formation, whilst the presence of twenty times as much methane has been either altogether ignored or passed over as relatively unimportant. Moreover, whereas the influence of temperature on the nature and sequence of the changes involved has received considerable attention, the equally important factor of time has been largely disregarded. We venture to think that the facts brought to light during the present investigation will go far to determine the relative importance of methane and acetylene as high temperature decomposition products.

Several years ago, one of us, in conjunction with Dr. D. S. Jerdan, proved that methane is the only hydrocarbon formed synthetically from its elements at temperatures between 1000° and 1200° (Trans., 1897, **71**, 41; 1901, **79**, 1042), and, although this conclusion has recently been doubted, it has been confirmed by a careful repetition of the original experiments, and derives additional support from the results of the present research.

The range of temperature covered by our experiments extends from about 500° up to nearly 1200°, and special attention has been paid to the influence of the time factor on the various decompositions. The main conclusions, which materially differ in several important respects from those of previous workers, are summarised in the following paragraphs:

(1) Methane, which is by far the most stable of the four hydrocarbons examined, is always a principal product of the decomposition of the other three, especially at temperatures above 800°. It decomposes for the main part *directly* into carbon and hydrogen, and the process, which is probably reversible at all temperatures, is (at least within the temperature range above indicated) chiefly a surface phenomenon.* The carbon deposited from methane is of a peculiarly hard and lustrous type, wholly different from the dull, soft variety yielded by the other three hydrocarbons, except in so far as part of the latter may arise as the result of the secondary decomposition of methane.

(2) The decomposition of the other three hydrocarbons is not chiefly a surface effect, but takes place throughout the main body of the gas.

(3) Acetylene is a principal product of the decompositions of ethylene, but not of either methane or ethane. The equation put forward by V. B. Lewes for the decomposition of ethylene is, however, disproved.

(4) At comparatively low temperatures, acetylene exhibits a strong tendency to polymerise, forming benzene, &c., so that whenever acetylene is a principal primary product in the decomposition of another hydrocarbon (for example, in the case of ethylene) there is always a marked secondary formation of aromatic hydrocarbons at low temperatures. This tendency to polymerise reaches a maximum probably somewhere between 600° and 700°, after which it diminishes rapidly as the temperature rises, and is but little in evidence above 1000°.

(5) Both acetylene and ethylene exhibit a certain tendency to combine with hydrogen at low temperatures, forming ethylene and ethane, but the importance of this factor, which is never very great, diminishes as the temperature rises, and is insignificant above 1000°.

(6) One of the principal factors operative at 800° and higher

---

* The conclusion as to the decomposition being chiefly a surface effect applies up to 1200°, and probably at still higher temperatures, which were not investigated. Presumably at very high temperatures, decomposition would (in part at least) take place throughout the main body of the gas itself; this is certainly the case in the electric arc (Bone and Jerdan).

temperatures is the direct "hydrogenation" of such residues as $\vdots CH$, $:CH_2$, and possibly $\cdot CH_3$ (which conceivably have a momentary separate existence during the dissolution process) to methane whenever the atmosphere is already rich in hydrogen. In this and in no other way can the phenomenally large production of methane during the decomposition of the other three hydrocarbons be accounted for. The assumption of this factor also explains the greatly superior stability of methane over the other hydrocarbons at all temperatures examined.

(7) Berthelot's theory of the mechanism of hydrocarbon decompositions, with its consequent assumption of the attainment of a complex state of equilibrium at each particular temperature, is finally disproved.

(8) The mode of decomposition of any particular hydrocarbon cannot be expressed by means of a single chemical equation as ordinarily employed. For whilst it may sometimes seem possible to apply a given equation such, for instance, as

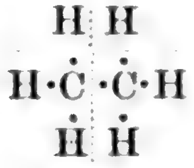
$$C_2H_6 = C_2H_4 + H_2 = C + CH_4 + H_2$$

to a particular case within certain rather narrow temperature limits, any attempt to extend the system invariably results in inconsistency and confusion.

(9) But whilst the rigid application of ordinary equations is, as a rule, inadmissible, it is not difficult to formulate a scheme based on the assumption set forth in paragraph (6), showing the chief causes at work and their modes of operation in any given case. The scheme applies more particularly to ethane, ethylene, and acetylene, since the decomposition of methane is, in the main, a direct resolution of the gas into its elements.

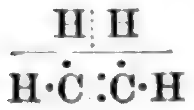
(10) In the cases of ethane and ethylene, it may be supposed that the *primary* effect of high temperature is to cause an elimination of hydrogen with a simultaneous loosening or dissolution of the bond between the carbon atoms, giving rise to (in the event of dissolution) residues such as $:CH_2$ and $\vdots CH$. These residues, which can only have a very fugitive separate existence, may subsequently either (*a*) form $H_2C{:}CH_2$ and $HC\vdots CH$, as the result of encounters with other similar residues, or (*b*) break down directly into carbon and hydrogen, or (*c*) be directly "hydrogenised" to methane in an atmosphere already rich in hydrogen. These three possibilities may all be realised simultaneously in the same decomposing gas in proportions dependent on the temperature, pressure, and amount of hydrogen present. The whole process may be represented by the following scheme, the dotted line indicating the tendency to dissolve the bond between

the carbon atoms which becomes actually effective at higher temperatures.*



$$\begin{matrix} H & H \\ H\cdot\dot{C} & \cdot\dot{C}\cdot H \\ \dot{H} & \dot{H} \end{matrix} = [2(\colon CH_2)+H_2] = \begin{cases} (a)\ C_2H_4+H_2. \\ (b)\ 2C+2H_2+H_2. \\ (c)\ \textit{plus}\ H_2=2CH_4 \end{cases}$$

Ethane.



$$\begin{matrix} H & H \\ \hline H\cdot\dot{C} & \colon\dot{C}\cdot H \end{matrix} = [2(\vdots CH)+H_2] = \begin{cases} (a)\ C_2H_2+H_2. \\ (b)\ 2C+H_2+H_2. \\ (c)\ \textit{plus}\ 2H_2=2CH_4. \end{cases}$$

Ethylene.

(11) In the case of acetylene, the main primary change may be either one of polymerisation or of dissolution, according to the temperature, and if the latter, it may be supposed that the molecule breaks down across the triple bond between the carbon atoms, giving rise to 2(⁝CH), and that these residues are subsequently either resolved into carbon and hydrogen or "hydrogenised," according to circumstances, thus:*

$$\underset{\substack{\downarrow \\ \text{Polymerisation.}}}{HC\vdots CH} = 2(\vdots CH) = \begin{cases} (a)\ 2C + H_2 \\ (b)\ \textit{plus}\ 3H_2 = 2CH_4 \end{cases}.$$

Incidentally, it may be observed that the rates of decomposition of these hydrocarbons are very much slower than their rates of combustion, and that therefore in the propagation of a flame through a homogeneous mixture of a hydrocarbon and oxygen, oxidation will probably take precedence of all other chemical phenomena.

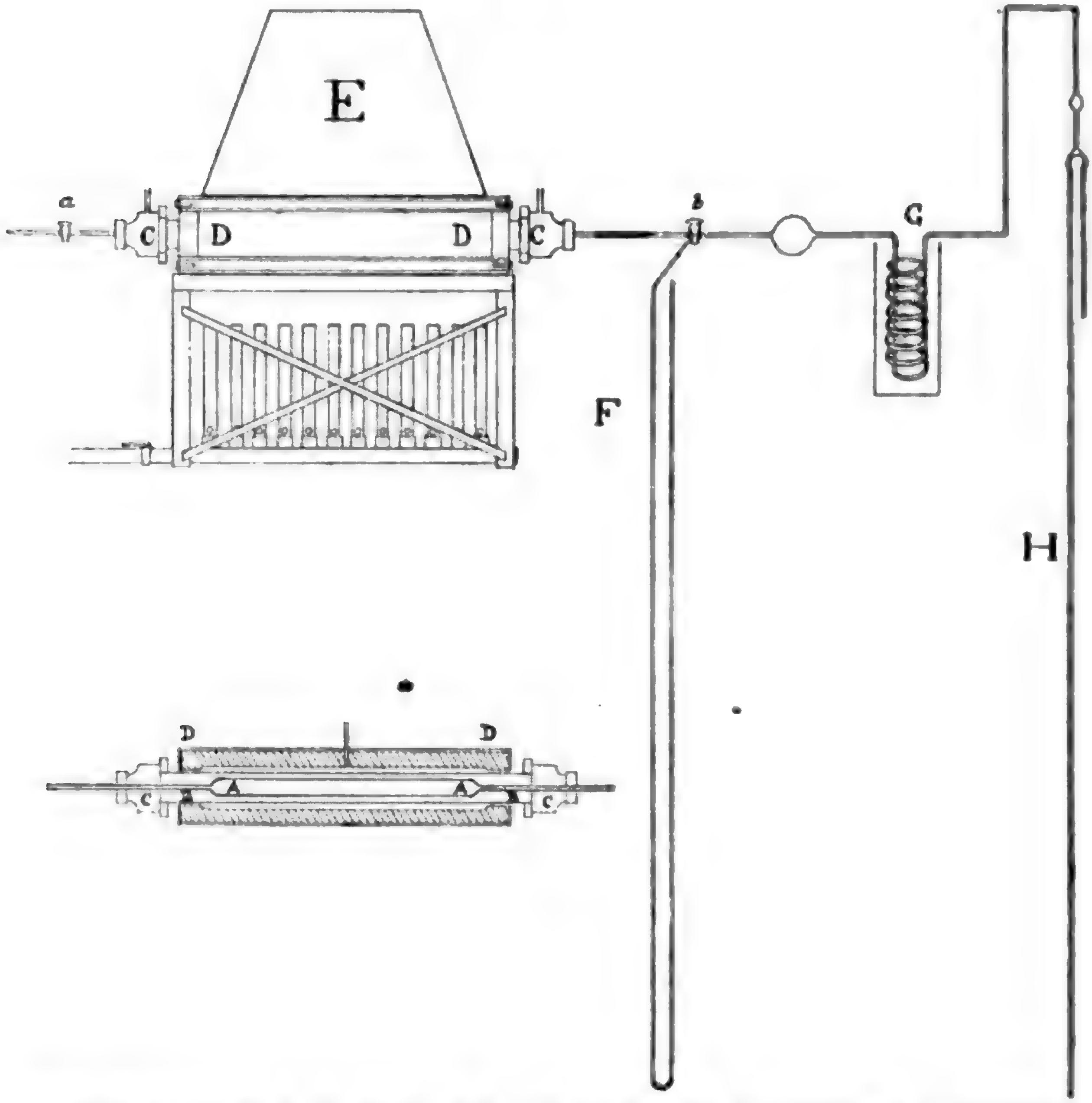
EXPERIMENTAL.

Apparatus and Methods.—The apparatus employed in the experiments above 700° consisted of an arrangement of two coaxial tubes of best Berlin porcelain, glazed within and without, similar to that used by Bone and Jerdan in their experiments on the direct union of carbon and hydrogen (Trans., 1897, **71**, 46), and is diagrammatically shown in Fig. 1. The inner tube, *AA* (length = 29 cm., 12 mm. internal and 16·5 mm. external diameter), terminated in narrow ends, each 16 cm. long and 2 mm. bore. It was held in position coaxially within the outer tube, *BB* (length = 50 cm., 24 mm. internal and 30 mm. external diameter), by means of two special brass end pieces, *CC*, provided with stuffing boxes packed with asbestos wool moistened with "Roman" cement, which rendered the joints between the two tubes quite gas-tight. These brass end pieces were provided with side-tubes, which permitted of a slow current of pure dry hydrogen being maintained through the annular space between the two porcelain tubes throughout each experiment, thereby both ensuring the even heating of the inner tube and protecting its contents from any contamination with the furnace gases. The tubes were heated mainly by radiation from the fireclay walls of the specially designed gas furnace (length = 35 cm.) containing thirteen powerful burners, with a draught induced by the iron chimney, *E*. The furnace was protected by means of thick screens of asbestos mill-board, and the gas supply was automatically controlled by means of a Stott governor. The temperature of the porcelain tubes was recorded by a Le Chatelier thermo-junction

---

* With regard to ethylene and acetylene, it is to be understood that changes of the kind indicated under (4) and (5), which do not involve a breaking down of the original molecule, may take place independently, but such changes are essentially low temperature effects.

Fig. 1.



The tube at a *leads to the drying tube and gas-holder; in circulation experiments to the large globe, &c.*

connected with a dead-beat galvanometer, and it could be kept practically constant (within a total variation of about 20°) for many hours together. The narrow ends of the inner tube, *AA*, projected some distance on either side beyond the furnace; one of these ends was connected, through the stopcock, *a*, and drying tubes containing calcium chloride, with a glass holder containing the gas under investigation; the other end communicated, through the three-way stopcock, *b*, with the capillary manometer, *F*, the spiral condenser, *G* (which was externally cooled by ice during each experiment), and the automatic Sprengel pump, *H*.

At the outset of an experiment, the porcelain tubes were heated to the desired maximum temperature, and the inner tube thoroughly exhausted. The tap *b* was thereupon closed, and by opening *a* the gas under investigation was admitted until the manometer indicated a pressure slightly above that of the outside atmosphere. The gas was then maintained at the experimental temperature for a definite period of time, during which pressure records could be taken at regular intervals, and, finally, by momentarily opening the tap *b*, a sample of the residual gas was instantly drawn over into the vacuous condenser and pump connexions, whence it was afterwards collected through the pump for analysis. After removal of the sample, the whole apparatus was again exhausted in readiness for the next experiment; in this way a series of consecutive experiments at a particular selected temperature could be made without cooling down the porcelain tubes.

The presence of aromatic hydrocarbons in the products was indicated by the appearance of a mist in the bulb of the spiral condenser when the tap *b* was opened.

Whilst the above represents the usual experimental procedure, it was subject to considerable variations for special reasons. By a slight modification of the apparatus, the action of heat on a flowing stream of the gas could be investigated. Also, the length of the inner tube was sometimes varied, and occasionally a tube of the same internal diameter as the one shown in the diagram, but without narrow ends, was used, in which case each end of the tube was fitted with a ground-glass joint secured by a short length of indiarubber tubing. When the influence of hot surfaces on the decomposition of methane was to be studied, the inner tube was packed with fragments of the selected solid, but otherwise no packing was employed.

A notable departure from the usual procedure was made at temperatures below 700°, where the rate of decomposition in a particular case was slow enough to admit of the employment of the "circulation" method devised by Bone and Wheeler (Trans., 1903, **83**, 1076). In such a case the apparatus was converted into a closed system by the insertion of a larger globe and a series of by-passed sampling tubes (for particulars of the arrangement see *Phil. Trans.*, 1906, *A*, **205**, 9), thus rendering it possible to operate on large volumes of the gas under examination, and to follow the course of its decomposition both by pressure records and a series of gas samples cut out at regular intervals without disturbing the experimental conditions.

Analysis of the Gases.—As the gaseous products often contained acetylene, ethylene, ethane, methane, and hydrogen as well as small quantities of carbon monoxide, formed by the reduction of the surface of the inner porcelain tube by carbon deposited on it at high temperatures,* special methods were adopted for the separate estimation of each constituent. For the estimation of ethane (if any) present, a portion of the gas remaining after the complete removal of acetylene, ethylene, and carbon monoxide was subjected to the action of "oxidised" palladium sponge at 100° until all the hydrogen was eliminated; the residual saturated hydrocarbon was subsequently exploded with excess of oxygen and the ratio C/A determined in the usual manner.

In recording the composition of the gaseous products in the various experiments, any small percentage of adventitious nitrogen or of carbon monoxide has been omitted; the tabulated results therefore give the percentage composition of the nitrogen- and carbon monoxide-free products.

Experiments with Methane.

The methane was prepared by the method described by Bone and Wheeler (Trans., 1902, **81**, 541); the ratio C/A obtained in an explosion-analysis was exactly 2·0, showing that the gas was quite free from hydrogen.

(*a*) Preliminary experiments showed that the rate of decomposition is inappreciable at temperatures below 700° unless a very large surface is exposed to the gas by packing the heated tube with some porous material. In one experiment at 785° (no "packing" in the tube) the gaseous products at the end of an hour contained no less than 91·6 per cent. of methane, the remainder being hydrogen without even a trace of acetylene. None of the other hydrocarbons investigated exhibited anything like so high a stability at this temperature.

Experiments at 1000°.—Comparative experiments at this temperature, in which the heated tube was used both with and without any special "packing," proved how largely the decomposition is a surface effect; indeed, we are of the opinion that it is entirely so.

---

* It is impossible to avoid a certain amount of reduction of the porcelain by carbon at temperatures above bright red heat.

(*b*) The following table refers to a typical series of experiments in which the gas was shut up in the heated tube (unpacked) at atmospheric pressure for periods of time varying from one to 60 minutes:

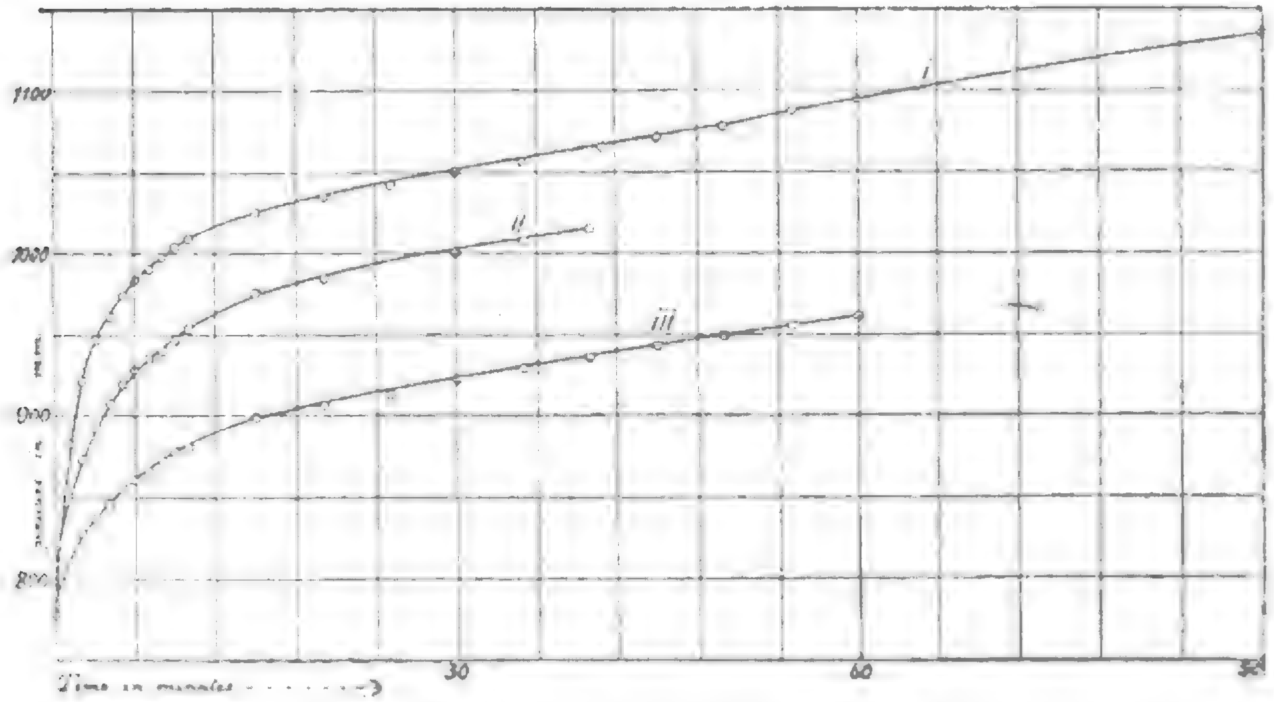
TABLE I.

Temperature		985°.	985°.	1000°.	985°.	1015°.
Duration of heating (mins.)		1.	5.	15.	30.	60.
Percentage composition of gaseous products.	Acetylene	0·5	0·5	nil	nil	nil
	Unsaturated hydrocarbons	0·3	0·5	1·3	0·35	nil
	Methane	90·4	75·4	65·25	62·85	48·2
	Hydrogen	8·8	23·6	33·3	36·8	51·2

It will be observed: (1) that the rate of decomposition, for an equal amount of surface exposed to the gas, was about sixty times greater at 985° than at 785°; (2) that the formation of acetylene or unsaturated hydrocarbon could only be detected so long as the methane concentration exceeded about 60 per cent., and (3) that with lower methane concentrations the gas continued to be directly resolved into its elements in contact with the hot walls of the tube. It should be added that, in harmony with (2), only at high methane concentrations was there any indication of the formation of aromatic hydrocarbons by the appearance of a slight mist in the bulb of the cooling worm when the tap leading out of the heated tube was opened.

(*c*) Further insight into the general character of the phenomena is gained by a comparison of the pressure curves (Fig. 2, ordinates = pressure in mm; abscissæ = time in minutes) obtained in a series of three experiments in which the gas, in the first instance undiluted, but in the two subsequent experiments diluted with either 1 or 3 vols. respectively of nitrogen, was introduced into the hot tube (unpacked) at initially nearly the same pressure. It may be remarked that in experiments of this kind it is absolutely necessary first of all to coat completely the walls of the hot tube with a layer of carbon deposited by methane in course of active decomposition, for otherwise changes in the surface conditions during an experiment would render the results valueless for comparative purposes. The curves obtained show that, especially in the case of the undiluted methane, the rate of decomposition is during the first few minutes proportional to some high power of the concentration, but that afterwards it rapidly approaches, and finally attains, a value corresponding to a reaction of the first order. The correct interpretation of these curves is, we think, to be found in the fact that they refer to a condition of things in which highly condensed layers of gas are decomposing in contact with a hot surface. Such layers would be formed instantaneously when the gas was first introduced into the hot vacuous tube, and rapid decomposition would at once ensue; the consequent outrush of hydrogen from the surface would speedily reduce the methane concentration not only in the surface layer, but also in the main body of the gas outside, thus setting up more normal conditions in the system. It is clear also that the formation of minute quantities of acetylene and unsaturated hydrocarbon (including benzene) is a circumstance associated with the initial "abnormal" period, the normal conditions corresponding with the direct resolution of the methane into carbon and hydrogen in contact with the hot surface.

FIG. 2.



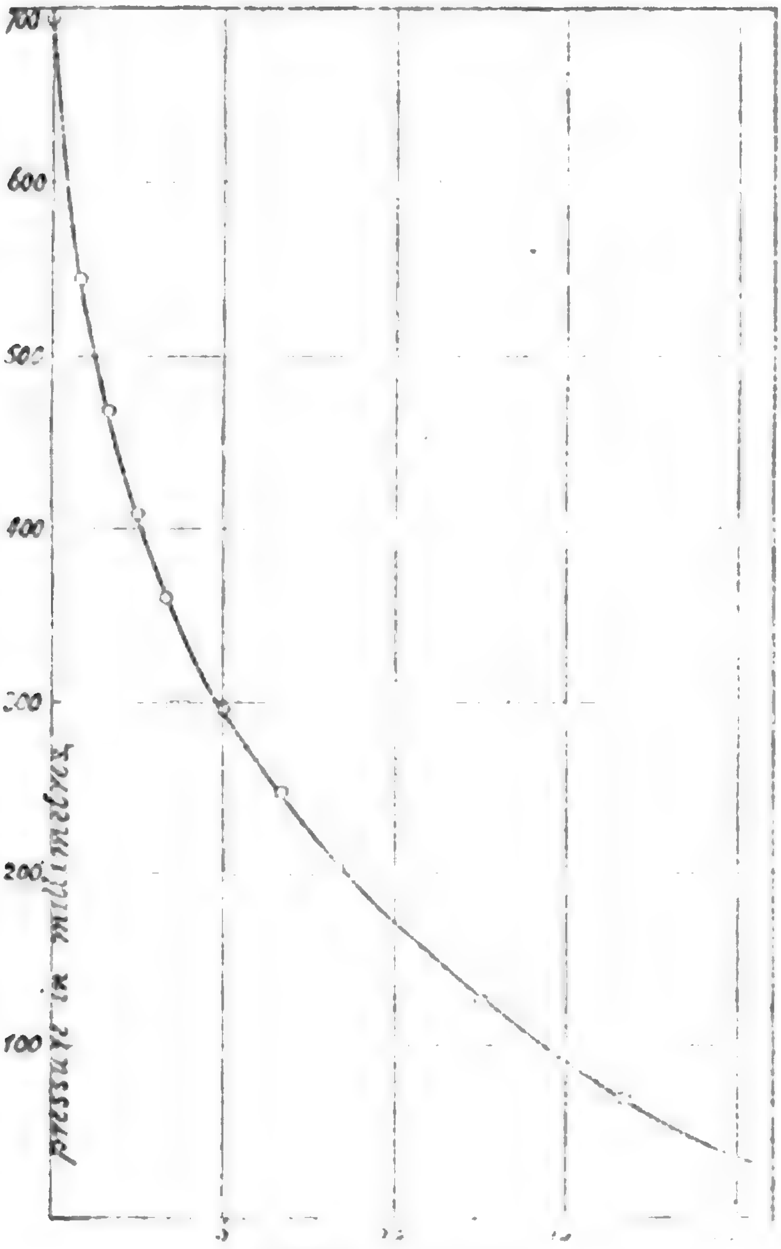
Curve I. *Undiluted methane.*
,, II. *Methane diluted with its own volume of nitrogen.*
,, III. ,, ,, ,, *three times its own volume of nitrogen.*

(*d*) The next experiment shows the effect of largely increasing the surface exposed to the gas. The hot tube was packed with fragments of quicklime *; the decomposition now became extremely rapid, the products containing only 1·9 per cent. of methane after twenty-five minutes, whilst at the end of an hour, when equilibrium was practically established, only 0·7 per cent. remained (temp. = 1030°). The final gases contained 2·8 per cent. of carbon monoxide, formed by the reduction of the surface exposed to the gas. The curve showing the methane concentrations during the first half of the experiment (Fig. 3, ordinates = pressure of methane in mm.; abscissæ = time in mins.) indicates a much more rapid setting up of "normal" conditions than in the previous experiments, where the surface exposed to the gas was very much smaller. After the third or fourth minute the

---

* The use of porous porcelain for this purpose was found to be inadmissible, owing to the readiness with which it is attacked and reduced by the methane (or possibly by the carbon deposited from methane) at this temperature. How strong this reducing action is may be gathered from the fact that in one experiment, in which the tube was packed with this material, the gases contained no less than

FIG. 3.



Time in minutes.

10·5 per cent. of carbon monoxide after 30 minutes and 22·5 per cent. after 60 minutes (nitrogen = 0·7 per cent. only). We do not know that this strong reducing action on porous porcelain has been noticed before. In similar experiments with quicklime the action was very slight, the gases containing only 2·8 per cent. of carbon monoxide after 60 minutes.

rate of decomposition assumed a value corresponding with a reaction of the first order, and this was steadily maintained until the end of the experiment. The following table gives two sets of values for the expression $1/t\log C_o/C_t$, one for the whole duration of the experiment, and the other in which C_o is taken as the methane concentration at the third minute:

TABLE II.

t. Minutes.	P. Total pressure in mm.	C. Methane concentration in mm.	$1/t\log C_o/C_t$.	
0	790·0	694·0	—	—
1	942·0	543·5	0·1062	—
2	1020·5	466·5	0·0862	—
3	1080·5	408·0	0·0769	0·0582
4	1129·5	360·5	0·0711	0·0560
6	1198·0	295·0	0·0619	0·0490
8	1249·0	246·5	0·0562	0·0462
10	1296·0	203·0	0·0539	0·0452
15	1382·0	125·0	0·0500	0·0440
20	1445·5	70·0	0·0498	0·0458
25	1493·0	28·5	0·0555	0·0528

Experiments at 1150—1160°.—The following typical series of experiments, in which the gas was initially admitted to the (unpacked) tube at 1150—1160° under atmospheric pressure, afford striking proof, not only of the extraordinarily great stability of methane as compared with other hydrocarbons examined at this temperature, but also of the fact that the "normal" decomposition does not involve the formation of acetylene. For, except during the first minute, not a trace of acetylene could be detected among the products, nor was there any indication of the formation of aromatic hydrocarbons. The gas was undoubtedly resolved directly into carbon and hydrogen in contact with the hot walls of the tube. The results of this series of experiments are tabulated below:

TABLE III.

Temperature	1150°	1150°	1160°.	1150—1160°.
Duration of heating (mins.)	1.	5.	60.	180.
Acetylene	0·5	nil	nil	nil
Methane	44·6	27·25	22·3	9·15
Hydrogen	54·9	72·25	77·7	90·85

Character of the Carbon obtained from Methane.—The form in which the carbon was deposited from the decomposing methane at all temperatures deserves special notice. It was entirely a surface deposit of a peculiarly hard and lustrous variety, almost metallic in appearance, and totally different from the dull, soft variety yielded by acetylene, or any of the other hydrocarbons examined under similar conditions.* This circumstance not only harmonises with the view that the decomposition of methane is, at these temperatures, a surface effect entirely, but is inconsistent with the supposition that the primary decomposition involves the formation of acetylene, for example, $2CH_4 = C_2H_2 + 3H_2$, which must now be regarded as untenable. Moreover, it seems probable that the peculiar properties of the "gas carbon" formed in the crown of the retorts during the manufacture of coal gas, as well as the characteristic metallic lustre of the coke obtained in coke-oven practice, where high temperatures prevail, are due to this "surface" decomposition of methane. The general character of the decomposition also, in a great measure, accounts for the comparatively feeble luminosity of the flame of methane.

Experiments with Ethane.

(*a*) *Circulation Experiments at* 675°.—After some preliminary trials, 675° was adopted as a suitable initial temperature, the apparatus being fitted with the necessary connexions for a "circulation" experiment, including a series of by-passed sampling tubes in order that samples of the gas might be shut off at intermediate periods during the experiment, without in any way altering the pressure in the apparatus or interrupting the course of chemical change. The apparatus so arranged had a capacity of about 3 litres. Pure ethane, prepared from zinc ethyl, was set circulating through the heated (unpacked) tube ($T = 675°$) at an initial pressure of 248 mm.; this low pressure, together with the fact that the temperature of the hot tube was well below that at which methane begins to decompose in similar circumstances, would, it was thought, make it easier to discover the character of the primary reaction. The gas decomposed fairly rapidly, the pressure in the apparatus increasing by more than 80 per cent. within three hours, after which it remained nearly constant. In the spiral condenser, which was kept at 0° throughout the experiment, there appeared a few minute crystals of naphthalene mingled with traces of a tarry substance, but curiously enough no benzene could be detected.

Analyses of samples of the gas (see table IV. below) shut off in the by-passed tubes at intermediate points during the experiment revealed the formation of much ethylene and hydrogen, but comparatively small quantities of acetylene during the initial stages, followed by a considerable accumulation of methane, at the expense of ethylene, towards the end of the process. Carbon was also deposited in the hot tube:

---

* Except, of course, in so far as the other hydrocarbons may yield the hard variety as the result of the secondary decomposition of methane.

TABLE IV.

Temperature = 675°. *Initial Pressure of Ethane* = 248 mm.

Time (hours)		½.	1½.	3.	6.
p_2/p_1*		1·47.	1·70.	(1·8).	1·87.
Percentage composition of gaseous products.	C_2H_2	4·1	5·1	2·8	1·9
	C_2H_4	24·7	24·1	16·4	0·7
	C_2H_6	34·7	9·8	7·3	2·0
	CH_4	8·4	19·9	32·9	54·5
	H_2	28·1	41·1	40·6	40·9

* Ratio of the pressure in the apparatus to the initial pressure.

On repeating the experiment, it was found that an initial pressure of 221 mm. (corresponding with 1·20 grams) of ethane ultimately gave rise to 207 mm. of hydrogen, 213 mm. of methane, 3 mm. of acetylene, as well as 0·4 gram (at least) of a soft, flaky variety of carbon and about 0·05 gram of almost pure naphthalene, but no benzene. At an intermediate point during the experiment, when about 86 per cent. (that is, 189 mm.) of the original ethane had disappeared, the gaseous products contained as much as 19 per cent. of ethylene.

The above facts are clearly inconsistent with Berthelot's view that the primary decomposition of ethane may be represented by the equation

$$2C_2H_6 = C_2H_2 + 2CH_4 + H_2,$$

or, indeed, with any other theory involving the prominence of acetylene among the initial products. On the other hand, they certainly suggest, and taken by themselves apart from any other evidence might almost seem to prove, that the sequence of changes may be represented by the following scheme:

$$C_2H_6 = C_2H_4 + H_2 = C + CH_4 + H_2.$$

But, as will be shown later, this cannot be considered as portraying the real mechanism of the process, although in a crude way it expresses its outward character.

(*b*) *Experiments at* 800°.—(1) At this temperature ethane decomposes so rapidly that the adoption of the "circulation" method was quite out of the question. Accordingly, we had to be content with shutting up the gas in the hot tube (unpacked) for definite periods of time, keeping a sharp look out for the appearance of any mist in the bulb of the spiral condenser when the products were finally allowed to escape out of the zone of reaction. In considering the results of the following typical series of experiments, it must be borne in mind that the rate of decomposition of methane under similar conditions was found to be negligible, except when the heating was prolonged beyond thirty minutes:

TABLE V.

Temperature	810°.	805°.	810—815°.	810°.	810—815°.
Time (mins.)	1.	5.	15.	30.	60.
Appearance in spiral condenser	Yellow mist and deposition of crystals.	White mist, no crystals.	No appearance of either mist or crystals.		
Percentage composition of gaseous products. C_2H_2	1·90	1·20	0·50	trace	nil
C_2H_4	11·20	4·40	0·75	nil	nil
C_2H_6	17·90	2·40	nil	nil	nil
CH_4	31·30	54·55	64·65	66·0	63·75
H_2	37·70	37·45	34·10	34·0	36·25
Ratio CH_4/H_2 in products.	0·83	1·46	1·90	1·94	1·75

It is evident from the composition of the gases at the end of a minute, not only that ethylene is still prominent among the primary products at this temperature, but also that, whilst acetylene and aromatic hydrocarbons could be detected, they were never present in sufficiently large amounts to be regarded as really important factors. The most striking feature about these results is, however, the rapid accumulation of methane in the products; thus, the ratio of methane to hydrogen increased from 0·83 at the end of a minute to as much as 1·94 at the end of thirty minutes, during which period all other products except carbon had entirely disappeared. So high a ratio as 1·94 is obviously inconsistent with the scheme

$$C_2H_6 = C_2H_4 + H_2 = C + CH_4 + H_2,$$

and for a long time we were quite unable to account for it. The supposition that it might be due to the secondary decomposition of aromatic hydrocarbons was at once disproved when submitted to the test of experiment. Several other possible explanations were similarly dismissed.

(2) Finally, we were compelled to look for a solution of the difficulty in some kind of change, whereby hydrogen disappears and methane is generated. A long search for such a process led to the discovery of a hitherto unsuspected and important factor in hydrocarbon decompositions, namely, the formation of methane by the direct hydrogenation of either gaseous carbon itself, or, more probably, of such residues as $\vdots CH$, $:CH_2$, or $\cdot CH_3$, which may conceivably arise by the initial breaking down of a hydrocarbon molecule in an atmosphere rich in hydrogen.

The proof that such a factor is really operative at high temperatures is furnished by the following comparative experiments on the relative amounts of methane formed when ethane, diluted to an equal degree with (*a*) nitrogen and (*b*) hydrogen, is completely decomposed under conditions precluding any sensible loss of methane. These conditions it was found were fulfilled by separately shutting up mixtures corresponding with $C_2H_6 + 3N_2$ and $C_2H_6 + 3H_2$ respectively at atmospheric pressure in the hot tube at 800° for an hour in each case. Four separate experiments were carried out with each of the two mixtures; the ethane was in all cases completely decomposed, the ultimate products consisting of carbon, hydrogen, and methane only, the percentage amounts of the last named being as follows:

Original mixture	Percentage methane obtained.	Mean.
$C_2H_6 + 3N_2$	18·5, 17·15, 18·3, 18·7	18·15
$C_2H_6 + 3H_2$	42·9, 38·0, 43·9, 40·15	41·25

$$\text{Ratio } \frac{41{\cdot}25}{18{\cdot}15} = 2{\cdot}27.$$

It is clear that with an inert gas, such as nitrogen, as the diluent, the ultimate result corresponded very nearly with the equation

$$C_2H_6 + 3N_2 = C + CH_4 + H_2 + 3N_2,$$

whereas, under similar conditions with the active hydrogen, about 80 per cent. of the carbon originally present appeared as methane in the products, as though the change had been principally

$$C_2H_6 + 3H_2 = 2CH_4 + 2H_2.$$

This striking difference can only be attributed to the operation of a cause such as the one indicated above, and, as will be shown later, the same thing also applies in the cases of both ethylene and acetylene, the theory may be accepted as having a solid basis of fact.

(*c*) *Experiments at* 1000°.—At this temperature we were operating under conditions admitting of the slow decomposition of methane, so that this product rapidly accumulated at first, but afterwards diminished in amount as the heating was continued, as the following typical series of experiments indicate:

TABLE VI.—*Temperature* = 1000°.

Time (mins.)		1.	5.	30.	180.
Percentage composition of gaseous products.	C_2H_2	2·5	0·55	0·50	0·3
	C_2H_4	6·9	1·80	0·2	nil
	C_2H_6	5·5	1·15	nil	nil
	CH_4	32·6	41·95	37·1	25·6
	H_2	52·5	54·55	61·2	74·1
Ratio CH_4/H_2		0·62	0·77	0·60	0·34

The fact that we were just able to discern the appearance of a white mist in the spiral condenser of the apparatus when the heating extended over one minute only, but none at all after five or more minutes, induced us to attempt an estimation of the amounts of aromatic hydrocarbons formed during the initial periods of the decomposition in the following special experiment.

Ten litres of ethane (13 grams) were passed through the heated tube (T = 1000°) at a speed such that each portion of the gas would not remain in the zone of reaction for longer than about half a minute. The issuing gases were passed through a weighed condenser externally cooled by ice. The amount of condensable hydrocarbons obtained did not, however, exceed 0·5 gram, or about 4 per cent. of the weight of the original ethane. This fact, together with the insignificant amounts of acetylene formed at this temperature, is clearly inconsistent with any form of "acetylene" theory, and also completely disposes of Berthelot's view that carbon arises only as the result of a long sequence of condensations in which heavy aromatic hydrocarbons play a principal rôle.

(*d*) *Experiments at* 1140—1185°.—Ethane is phenomenally unstable at this temperature, being scarcely able to survive a single rapid passage through the hot tube. The following results show that at the end of five minutes nothing remained besides carbon, hydrogen, and methane, the latter undergoing fairly rapid resolution into its elements. The large amount of methane at the end of five minutes is, from our point of view, a very significant feature of the decomposition:

TABLE VII.

Temperature		1140—1150°.	1150—1180°.	1175°.	1180—1185°.
Time (mins.)		5.	15.	30.	60.
Percentage composition of gaseous products.	C_2H_2	trace	nil	nil	nil
	CH_4	27·0	12·75	10·9	6·0
	H_2	73·0	87·25	89·1	94·0

Experiments with Ethylene.

Experiments at 570—580°.—At this temperature the gas changed slowly enough to enable us to bring the "circulation" apparatus, with its by-passed sample tubes, into operation. The initial pressure of the gas was 365 mm.; the heated tube was kept at 570° to 580°, and the gas rapidly circulated in the apparatus during two and a-half hours. The first of the intermediate samples was shut up within a few minutes of the commencement of the experiment, after about one-fourth of the original ethylene had decomposed; there was a slight fall in pressure in the apparatus as the experiment proceeded, and the course of the decomposition was marked by the expulsion of brown vapours from the hot tube. These vapours condensed, forming a viscous tar in the spiral condenser; very little carbon was deposited in the hot tube (about 0·011 gram only, or 0·75 per cent. of the weight of the carbon in the original gas). The results of the experiments will be better understood if the compositions of the gases at various periods are expressed, not in percentages as usual, but in terms of the actual partial pressures of the several constituents under constant volume, as shown on p. 1217.

The phenomena at this temperature are evidently very complex. Acetylene, ethane, methane, hydrogen, and aromatic hydrocarbons are all produced in quantity, but the amount of carbon which actually separates is negligibly small. It is to be particularly observed (1) that whereas methane rapidly and continuously accumulated during the experiment, the hydrogen accumulated up to a certain point only (60 mins.), after which it diminished slightly; (2) that the quantity of acetylene formed exceeded that met with in the experiments upon ethane, and at the end of the first minute amounted to as much as about 12 per cent. of the gases present, and (3) that the amount of carbon in the gases progressively diminished during the experiment until finally it was just half that contained in the original ethylene,

TABLE VIII.—*Temperature* = 570—580°. *Initial Partial Pressure of* C_2H_4 = 365 *mm.* = 730 *Units of Carbon.*

Sample No.		1.	2.	3.	4.	5.	6.	7.
Time (mins.)		2.	15.	30.	45.	60.	75.	150.
Partial pressures of gaseous products in mm.	C_2H_4	272·5	177·0	143·0	120·0	104·5	94·0	83·5
	C_2H_2	43·0	26·5	20·5	22·5	26·5	31·0	23·0
	C_2H_6	12·8	28·7	29·7	29·4	27·3	24·0	9·9
	CH_4	16·1	54·6	67·5	77·1	90·0	95·6	132·8
	H_2	17·9	72·9	93·1	101·0	102·0	97·4	93·0
Total pressure in mm...		362·5	359·0	354	351	350	342	342
Units of carbon in gases		672·7	519	454	421	406	393	365

a circumstance which indicates a continuous formation of aromatic hydrocarbons, mainly due to the polymerisation of acetylene or ⫶CH residues. In respect of (3), it is interesting to note how great is the contrast between the behaviour of ethane and ethylene at low temperatures, for whereas it was found that ethane ultimately yielded much carbon and very little aromatic hydrocarbons as it slowly decomposed at 675°, quite the reverse was observed in the case of ethylene. This difference is to be attributed to the fact that acetylene is one of the principal primary products in the decomposition of ethylene at low temperatures, whereas it is never a prominent factor in the case of ethane.

But whilst we agree with Lewes in regarding acetylene as a primary product of the decomposition of ethylene, the large accumulation of hydrogen in the above experiment *without* a corresponding separation of carbon at once disposes of his contention that the main decomposition may be represented by the equation

$$3C_2H_4 = 2C_2H_2 + 2CH_4,$$

because, in such a case, free hydrogen could only arise by the secondary resolution of the acetylene into its elements. Moreover, during the first thirty minutes of the experiment, the rate of accumulation of methane was only about one-third of the rate of disappearance of the ethylene,* instead of two-thirds of this rate, as demanded by Lewes' equation.

---

* During the interval between 0 and 30 minutes, 222 mm. of ethylene disappeared, but only 67·5 mm. of methane were produced.

The experiment also proves that the equation

$$C_2H_4 = C + CH_4$$

does not represent the main change at this temperature. This may at first sight seem inconsistent with what has been said respecting the decomposition of ethane at low temperatures, but the apparent inconsistency only emphasises the hopelessness of attempting to express the mechanism of these processes by means of ordinary chemical equations, and the necessity of regarding the phenomena from the standpoint advocated in this paper.

Experiments at 700—720°.—The results of two experiments at this temperature, with the apparatus set up in the ordinary way (that is, without the circulation arrangements), may be quoted in support of the foregoing argument, as follows:

Temperature		720°.	700°.
Time (mins.)		10.	30.
Percentage composition of gaseous products.	C_2H_2	3·75	2·4
	Benzene, &c.	1·25	traces
	C_2H_4	63·20	27·1
	C_2H_6	8·35	12·0
	CH_4	20·1	37·1
	H_2	3·35	21·3

Experiments at 800°.—(*a*) The chief interest of this series of experiments lies in the fact that the conditions precluded any appreciable decomposition of methane during the time required (fifteen minutes) to effect the disappearance of 90 per cent. of the original ethylene. There was a small increase in pressure during the first five minutes (namely, 750—790 mm.), after which it remained practically constant. The percentage compositions of the gaseous products are shown below:

TABLE IX.

Time (mins.)		1.	5.	15.	30.
Percentage Composition of gaseous products.	C_2H_2	3·00	23·90	3·85	nil
	C_2H_4	57·25	1·40	9·65	0·9
	C_2H_6	3·25	5·00	1·30	nil
	CH_4	29·40	53·40	64·45	67·7
	H_2	7·10	17·00	20·75	31·4

Comparing these results with those obtained at 570°, it may be observed (1) that there was a much larger separation of carbon and a smaller formation of aromatic hydrocarbons at the higher temperature, and (2) that, whilst both acetylene and ethane were still produced, although to a less extent than at 570°, there was a much larger formation of methane, the ratio of methane to hydrogen never falling below

3·0 as compared with usually less than 1·0 at the lower temperature. This is probably due to the direct hydrogenation of such residues as $:CH_2$ or $\vdots CH$, which certainly comes prominently into play at this temperature, as the following experiments prove.

(*b*) In these experiments, mixtures corresponding with $C_2H_4 + 3N_2$ and $C_2H_4 + 3H_2$ respectively were separately maintained at 800° for an hour in the same apparatus, and the methane in the final products subsequently determined. The duration of the heating sufficed not only to decompose the whole of the original ethylene in each case, but also to destroy any acetylene, ethane, or aromatic products, whilst practically the whole of the methane produced would survive. The following statement as to the percentages of amounts of methane obtained in four different experiments with each of the two mixtures proves how remarkably active hydrogen is at this temperature :

		Percentage of methane found.	Mean.
Original mixture	$C_2H_4 + 3N_2$ ……	15·45, 13·7, 13·4, 12·65………	13·8
	$C_2H_4 + 3H_2$ ……	42·6, 40·86, 44·3, 46·36………	43·5

$$\text{Ratio } \frac{43\cdot5}{13\cdot8} = 3\cdot15.$$

Experiments at 950°.—At this temperature 90 per cent. of the ethylene decomposed within a minute, and scarcely any of it survived after fifteen minutes. Much carbon separated, and the production of aromatic hydrocarbons was correspondingly small. It will be observed, from the table of results given below, (1) that acetylene was detected in the products after one and five minutes, but not subsequently, and (2) that the methane/hydrogen ratio in the products never exceeded 1·65, and rapidly diminished as the experiment was prolonged, a circumstance due to the continuous secondary decomposition of the methane, which was accompanied by a steady rise in pressure in the apparatus, namely, from about 750 to 950 mm. :

TABLE X. *Temperature* = 950°.

Time (mins.) ………		1.	5.	15.	30.	60.
Percentage composition of gaseous products	C_2H_2……	3·50	0·35	trace	trace	nil
	C_2H_4……	8·70	1·65	1·10	trace	nil
	CH_4 ……	54·75	48·35	44·75	38·20	71·9
	H_2………	33·10	49·65	54·15	61·80	28·1

N.B.—No ethane could be detected in the products.

An attempt was made to estimate the yield of aromatic hydrocarbons at this temperature by passing 10 litres of ethylene through the hot tube of the apparatus at a rate corresponding with a period of one and a-half minutes' heating for each successive portion of the gas. The results showed that not more than about 4 per cent. of the gas was converted into condensable products.

Experiments at 1180°.—The following series of experiments show little else than the rapid and complete resolution of ethylene into carbon, hydrogen, and methane at this temperature. Incidentally, also, the relatively great stability of methane is again strikingly demonstrated. Moreover, as might be expected, the formation of aromatic hydrocarbons was negligibly small:

TABLE XI. *Temperature* = 1180°.

Time (mins.)		5.	15.	20.	60.	240.
Percentage composition of gaseous products.	C_2H_2	0·50	trace	trace	trace	nil
	C_2H_4	1·75	0·70	nil	nil	nil
	CH_4	25·20	23·35	20·9	16·1	5·8
	H_2	72·55	75·95	79·1	83·9	94·2

Experiments with Acetylene.

Experiments at 480—500°.—A "circulation" experiment proved that the principal change at this temperature is, as might be expected, one of polymerisation. The gas was circulated over a surface composed of fragments of porous porcelain contained in a short Jena glass combustion tube heated to the required temperature in a Lothar Meyer constant temperature furnace. The total capacity of the apparatus was 3550 c.c., that of the heated tube about 100 c.c., and each circuit was completed in about forty-five minutes.

Starting "all cold" with a pressure of 500 mm. of acetylene, the temperature of the furnace was slowly raised to 440° in two and a-half hours, and to 480° by the end of five hours, the pressure falling to 430 mm. during this period. The experiment was continued for fifteen hours' longer, with the following results:

Time in hours.	Temp.	Pressure mm.
0 to 5	15 to 480°	500 to 430
6	491	399
7	493	382
8	492	360
9	493	342
10	492	324
11	490°	308
12	488	295
14	486	270
16	482	249
17	480	243
20	480	213

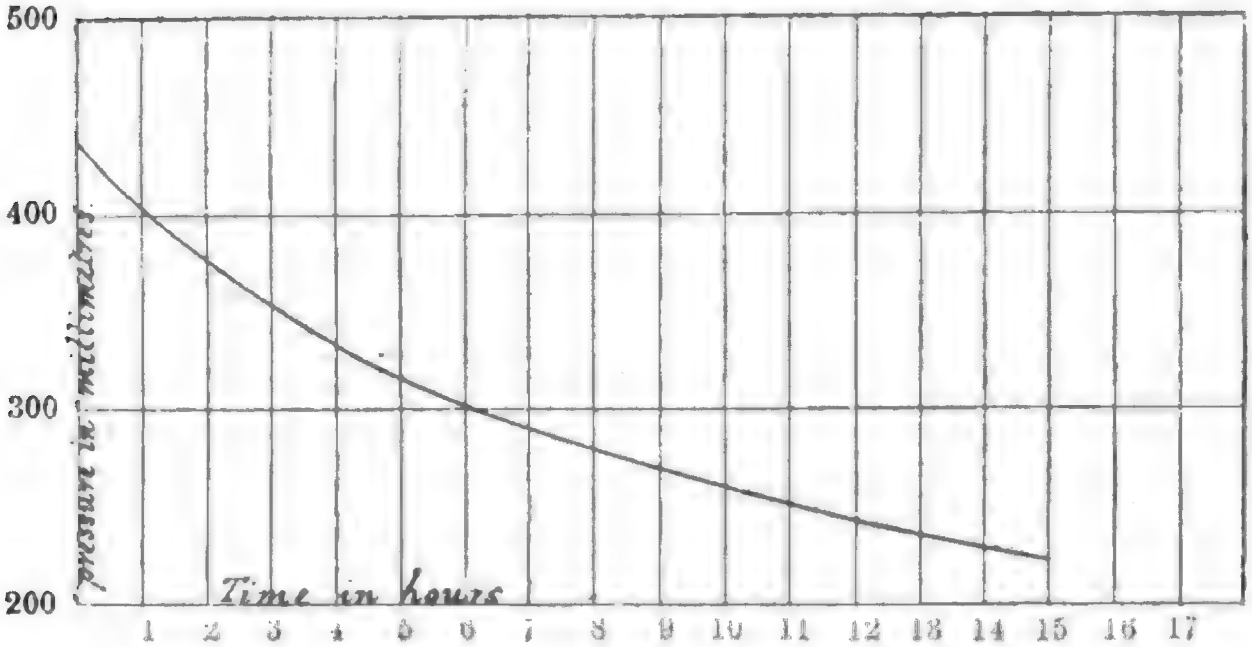
The pressure curve, for the period five to twenty hours, is reproduced in Fig. 4. Analysis showed that the residual 213 mm. of gas at the end of the experiment comprised:

$C_2H_2 = 88$, $C_2H_4 = 29$, $C_2H_6 = 32$, $CH_4 = 16$, and $H_2 = 48$ mm.

It would therefore appear that of the 412 mm. of acetylene which disappeared during the experiment, about 195 mm. (or 48 per cent.) had polymerised, 160 mm. (or 39 per cent.) had decomposed into carbon and hydrogen, whilst the remaining 57 mm. had been "hydrogenised," yielding ethylene, ethane, and methane.

With regard to the "condensed" products, the whole of the porous porcelain in the heated tube was coloured dark brown or black during the experiment, and, on extraction with chloroform in a Soxhlet apparatus, tarry matter was removed, leaving the surface black by reason of carbon impregnation. In the spiral condenser of the apparatus, which had been externally cooled with solid carbon dioxide throughout the experiment, a few drops of a limpid liquid with an aromatic odour and a green tinge had collected.

FIG. 4.



Experiments at 650°.—A similar "circulation" experiment was made at 650°. Starting with the cold reaction tube and a pressure of 510 mm., the temperature of the furnace was raised to 650° in an hour, during which the pressure fell to 330 mm. The experiment was continued for seven and a-half hours longer, at the end of which the pressure was 154 mm. Brown vapours were continuously expelled from the hot tube, and condensed in the cooled spiral. The pressure records were as follows:

Time in hours.	Temp.	Pressure mm.
0	15°	510
½	500	475
1	620	333
1½	640	275
2	640	249
2½	642	217
3	650°	200
4	643	180
5	647	172
6	647	168
8½	653	154

The residual 154 mm. of gas comprised:

$C_2H_2 = 19$, $C_2H_4 = 15$, $C_2H_6 = 2$, $CH_4 = 45$, and $H_2 = 70$ mm.

The weight of acetylene originally charged into the apparatus was 2·59 grams (that is, 2·39 carbon, and 0·20 hydrogen). Of this, 1·56 grams (or about 60 per cent.) polymerised, 0·75 gram, or as nearly as possible 30 per cent., was resolved into carbon and hydrogen, the remaining 10 per cent. appearing as "hydrogenised" products, that is, as ethane, ethylene, and methane.

Experiments at 800°.—(1) The gas decomposed so rapidly at this temperature that the "circulation" method was abandoned in favour of the ordinary arrangement of the apparatus. Moreover, except when the gas was largely diluted with nitrogen or hydrogen, it always "flashed" as soon as it entered the hot vacuous tube, so that its temperature must momentarily have been considerably higher than was recorded by the pyrometer. The greater part of the gas was undoubtedly decomposed during this momentary "flashing," but at the end of a minute there still remained about 25 per cent. of acetylene undergoing more or less rapid change. The results of a typical series of experiments are tabulated below:

TABLE XII. *Temperature* = 795°—800°.

Time (mins.)		1.	5.	15.	60.
Percentage composition of gaseous products.	H_2	25·9	7·3	1·35	nil
	C_2H_2	4 2	2·7	nil	nil
	C_2H_4	2·65	0·7	nil	nil
	C_2H_6	15·00	35·3	37·65	43·0
	CH_4	52·25	54·0	61·00	57·0

The appearance of a mist in the spiral condenser in the one minute experiment showed that polymerisation still occurs at this temperature, but owing to the "flashing" of the gas the conditions did not admit of any quantitative determination of the relative amount of gas so affected; it was, however, quite small, although there can be no doubt that it would have been much larger had no "flashing" occurred.

The most important feature of the above experiment is the large formation of methane, especially during the quiet decomposition which supervened after the "flashing" had subsided, and when the atmosphere was rich in hydrogen. The fact that the final products obtained after sixty minutes contained no less than 43 per cent. of methane is difficult to explain, except on the supposition of a direct "hydrogenation" of ⋮CH residues, formed by the initial breaking down of acetylene molecules across the triple bond between the carbon atoms.

(2) The above supposition was confirmed by a series of comparative experiments, in which mixtures corresponding with $C_2H_2 + 3N_2$ and $C_2H_2 + 3H_2$ respectively were kept in the hot tube at 800° for an hour, and the percentage of methane in the products determined. The results of four different experiments with each mixture are given below, and need no further comment:

		Percentage of methane found.	Mean.
Original mixture	$C_2H_2 + 3N_2$	6·9, 5·05, 5·7, 5·0......	5·65
	$C_2H_2 + 3H_2$	26·75, 25·0, 30·4, 27·3......	27·35

(3) Some reference to the phenomenon of "flashing" may be appropriately made in this connexion. Lewes claims for acetylene the peculiar property of what may be termed "incandescent decomposition" at high temperatures, which he regards as the sole cause of the luminosity of hydrocarbon flames. Haber, on the other hand, has denied that acetylene exhibits this property, except when mixed with small quantities of oxygen. So far as our own experiments are concerned, it should be stated that, whilst entirely dissenting from the acetylene theory of luminosity, which is not at present under discussion, we agree with Lewes in regarding the luminous decomposition of acetylene at high temperatures as a property of the gas itself, and in no way dependent on the presence of oxygen.

Experiments at Higher Temperatures.—The results of numerous experiments both at 1000° and 1100—1150° showed that the amount of polymerisation diminished, and the direct decomposition into carbon and hydrogen increased, as the temperature was raised. But, at the same time, considerable quantities of methane still appeared in the products, and it is significant that the maximum percentage of methane always nearly coincided with the disappearance of the last traces of acetylene. The large formation of methane, which greatly exceeded the equilibrium proportions at these temperatures, must be attributed to direct "hydrogenation" of ⋮CH residues. The results of two typical series of experiments are recorded on page 1224.

TABLE XIII. *Temperature* = 1000°.

Time (mins.).		1.	5.	60.
Percentage composition of gaseous products.	C_2H_2	13·85	1·85	nil
	C_2H_4	2·05	0·35	nil
	CH_4	19·10	20·65	14·75
	H_2	65·00	77·15	85·25

TABLE XIV. *Temperature* = 1120—1150°.

Time (mins.)		1.	5.	15.	75.	180.
Percentage composition of gaseous products.	C_2H_2	10.0	0·3	nil	nil	nil
	C_2H_4	2·0	nil	nil	nil	nil
	CH_4	16·0	21·3	16·1	7·75	3·0
	H_2	72·0	78·4	83·9	92·25	97·0

Comparative Experiments on the Relative Amounts of Polymerisation at Different Temperatures.

As it seemed desirable to estimate the relative amounts of polymerisation at different temperatures between 800° and 1150° under conditions calculated to eliminate as far as possible the effects of "flashing" already referred to, comparative experiments were made in the following manner. The porcelain tube of the apparatus was first of all heated to the desired temperature, and thoroughly exhausted. Acetylene was then admitted, and, as soon as the initial disturbance due to "flashing" had subsided, the pump was set working so as to draw a continuous stream of gas at a constant rate of about 4 litres per hour through the apparatus. In this way it was found that, except at the moment of the initial admission of the gas into the hot vacuous tube, no "flashing" occurred, the gas undergoing quiet decomposition as it passed through the zone of high temperature. Practically the whole of the acetylene was decomposed in each experiment; the amounts of polymerisation observed, as well as the compositions of the gaseous products, are tabulated on p. 1225. Attention is directed to the large amounts of methane formed.

TABLE XV.

Temperature		800°.	1000°.	1150°.
v_2/v_1*		0·59.	0·66.	0·77.
Percentage acetylene polymerised		19.	7·5.	5·0.
Percentage composition of gaseous products.	C_2H_2	1·35	1·55	nil
	C_2H_4	0·45	2·60	nil
	C_2H_6	0·50	nil	nil
	CH_4	34·20	36·00	23·45
	H_2	63·50	59·85	76·55

* The ratio of the volume of the gaseous products to that of the original gas.

These facts taken in conjunction with the results of the two circulation experiments at lower temperatures, indicate that the range of temperature most favourable to polymerisation lies between 600° and 700°, the tendency to this kind of change rapidly diminishes as the temperature is further raised.

The investigation is being extended to the higher members of the paraffin and other series of hydrocarbons; it is also our intention to examine further the conditions most favourable to the formation of naphthalene in these decompositions.

In conclusion we desire to express our indebtedness to the Government Grant Committee of the Royal Society for repeated grants towards the expenses of the research, and also to Dr. D. S. Jerdan, for valuable aid during its initial stages.

DEPARTMENT OF FUEL AND METALLURGY,
THE UNIVERSITY OF LEEDS.

CHEMICAL DEPARTMENT,
MANCHESTER UNIVERSITY.

CXVIII.—*The Effect of Constitution on the Optical Activity of Nitrogen Compounds.*

By REGINALD WILLIAM EVERATT, B.Sc.

SINCE *a*-phenylbenzylmethylallylammonium iodide was first resolved by Pope and Peachey (Trans., 1899, **75**, 1127) into dextro- and lævo-rotatory forms in which the activity was due to the asymmetry of the quinquevalent nitrogen atom, a considerable number of substituted ammonium iodides of the general type *a b c d* NI., where *a b c d* are different alkyl groups, have been similarly resolved into their optical isomerides and their physical constants measured and tabulated.

In a paper by Miss M. B. Thomas and H. O. Jones (Trans., 1906, **89**, 280), the values of the rotatory powers of ten substituted ammonium iodides were determined. These compounds formed two sets of five, all owing their activity to an asymmetric nitrogen atom attached to four alkyl groups. One set consisted of compounds containing the phenyl, methyl, and benzyl groups together with one of the following groups: ethyl, *n*- or *iso*-propyl, *iso*butyl, or *iso*amyl. The other set differed in that the benzyl group was replaced by the allyl group.

More recently, a third set has been added to these by Jones and Hill (Trans., 1908, **93**, 295). This set consists of iodides containing the groups *p*-bromophenyl, methyl, and allyl together with one of the homologous groups: ethyl, *n*- or *iso*-propyl, *iso*butyl, or *iso*amyl.

The results obtained were throughout discussed with reference to the application of Guye's hypothesis to the quinquevalent nitrogen atom, but it was decided that further data were necessary before deciding how far the hypothesis applied thereto.

The purpose of the present investigation was to provide further data and to render the above series more complete by preparing and resolving certain of these compounds containing the *n*-butyl group, namely, phenylmethyl-*n*-butylallylammonium iodide, *p*-bromophenylmethyl-*n*-butylallylammonium iodide, and *p*-bromophenylbenzylmethyl-*n*-butylammonium iodide. The last of these was also required for comparison with the corresponding unbrominated compound resolved by Wedekind and Fröhlich (*Ber.*, 1907, **40**, 1646). *p*-Bromophenylbenzylmethylallylammonium iodide was also prepared and resolved with a view to ascertaining its relation to the unbrominated analogue of Pope and Peachey already mentioned, and also to the remaining members of the group of brominated compounds already prepared.

The results of this investigation and their relation to those previously obtained are summarised at the conclusion of this paper. The method used for the resolution of these compounds was that of Pope and Peachey, and consisted in fractional crystallisation of the *d*-camphorsulphonate or *d*-bromocamphorsulphonate of the base from a suitable solvent. In one case, however, resolution was effected by use of *d*-tartaric and *d*-camphoric acids; the latter has not been previously used in this connexion. All measurements were made in a 2-dcm. tube. In investigating the effect of temperature on the molecular rotatory power, the densities of the solutions used were taken as identical with those of water at the same temperature, whilst the values of $[M]_D$ for the acidic ions are those given by Thomas and Jones (Trans., 1906, **89**, 284 *et seq.*).

Phenylmethyl-n-*butylallylammonium Iodide.*

Methyl-*n*-butylaniline was prepared in the manner already described by Wedekind and Fröhlich (*Ber.*, 1907, **40**, 1646). The fraction collected boiled at 236—239°.

Phenylmethyl-n-*butylallylammonium iodide* was prepared by mixing methyl-*n*-butylaniline and allyl iodide in molecular proportions. The mixture slowly deposited crystals, and at the end of sixteen hours was quite solid and crystalline. A portion was dissolved in hot alcohol and precipitated by the cautious addition of ether. After several repetitions of this procedure, the iodide was obtained in fine colourless needles melting at 80—81° if heated rapidly:

0·245 gave 0·1722 AgI. I = 37·98.

$C_{14}H_{22}NI$ requires I = 38·31 per cent.

Phenylmethyl-n-*butylallylammonium* d-*camphorsulphonate* was prepared by boiling equivalent quantities of phenylmethyl-*n*-butylallylammonium iodide and silver *d*-camphorsulphonate with moist ethyl acetate. The silver salt was finely powdered and covered with ethyl acetate. Two or three drops of water were added, and the whole heated to boiling in a small flask over the water-bath. The substituted ammonium iodide was then added in successive small quantities, shaking well after each addition. The precipitated silver iodide was collected, and the filtrate evaporated as far as possible on the water-bath; on allowing the residue to stand in a vacuum over sulphuric acid for a few days, it became crystalline, although largely contaminated with metallic silver. Many attempts to recrystallise the salt were made; alcohol, acetone, ethyl acetate, ethylal, methylal, benzene, toluene, and other solvents being used both alone and as mixtures. In every case the camphorsulphonate separated from the solution as an oil, and a similar result followed when ether was added slowly to any of the above solutions. Hence the attempted resolution by this method was abandoned.

Phenylmethyl-n-*butylallylammonium* d-*bromocamphorsulphonate* was prepared in a similar manner from equivalent quantities of the iodide and silver *d*-bromocamphorsulphonate. After evaporating the ethyl acetate, a dark viscid mass remained, which soon became crystalline on standing in a desiccator. It was dissolved in hot acetone, but could not be obtained crystalline from this solvent. When ether was cautiously added to its solution in ethyl acetate, crystals were slowly deposited, and, after two such recrystallisations, it was found possible to recrystallise it from hot acetone.

The salt of the dextro-rotatory base was thus obtained in clusters of fine colourless needles melting, if heated rapidly, at 149—150°:

0·1825 gave 0·3731 CO_2 and 0·1174 H_2O. C = 55·73; H = 7·14.
$C_{24}H_{36}O_4NBrS$ requires C = 56·03; H = 7·07 per cent.

The rotatory power gradually increased, and became constant after seven recrystallisations.

After seven recrystallisations, 0·1326 gram dissolved in 13·9055 grams of water gave a_D 1·34° at 14°; hence $[a]_D$ 70·3° and $[M]_D$ 361·3°.

After nine recrystallisations, 0·1264 gram in 11·1376 grams of water gave a_D 1·59° at 14°; hence $[a]_D$ 70° and $[M]_D$ 359·8°.

Hence the mean value for the basic ion at 14° is 85·6°.

The effect of temperature change on the rotatory power of the solution of the bromocamphorsulphonate was also investigated, and as usual proved to be very slight. The solution used contained 0·1674 gram of the salt in 16·2877 grams of water.

t.	a_D.	$[a]_D$.	$[M]_D$.	$[M]_D$ for basic ion.
2°	1·435°	69·81°	358·8°	89·3°
11	1·44	70·06	360·1	87·1
20	1·445	70·33	361·5	84·5
30	1·45	70·82	364·0	82·0
41	1·46	71·62	368·13	82·0
50	1·47	72·36	371·9	80·9

d-*Phenylmethyl*-n-*butylallylammonium iodide* was precipitated from the aqueous solution of the bromocamphorsulphonate by the addition of solid potassium iodide. The iodide crystallised slowly in small prisms melting at 79—80°. After recrystallisation from cold alcohol and ether, the salt melted at 80°. A mixture of the active and inactive iodides also melted at 80°.

Determination of its rotatory power in alcohol gave the following results:

0·1692 gram in 13·2126 grams of alcohol (density of solution = 0·809) gave a_D 0·66° at 15°; hence $[a]_D$ 31·78° and $[M]_D$ 105·19°.

0·1846 gram in 12·0115 grams of alcohol (density of solution = 0·81) gave a_D 0·79° at 15°; hence $[a]_D$ 31·72° and $[M]_D$ 104·99°.

The mean value is accordingly $[M]_D$ 105·09°.

The active iodide was readily soluble in chloroform, and a determination of its rotatory power showed that it racemised rapidly in this solvent.

Thus 0·1316 gram of the iodide in 18·5623 grams of chloroform (density of solution = 1·486) gave, ten minutes after making up, a_D 0·72° at 14°; hence $[a]_D$ 34·17° and $[M]_D$ 113·1°.

After one hour, a_D 0·53°, whence $[a]_D$ 25·15° and $[M]_D$ 83·25°.
,, two hours, a_D 0·38° ,, $[a]_D$ 18·03° ,, $[M]_D$ 59·68°.
,, four ,, a_D 0·21° ,, $[a]_D$ 9·97° ,, $[M]_D$ 33°.
,, six ,, a_D 0·10° ,, $[a]_D$ 4·75° ,, $[M]_D$ 15·7°.

At the end of nine hours, the solution was found to be inactive. By extrapolation from the curve, the value of $[M]_D$ at the instant of making up the solution is 123°.

A second determination in chloroform solution was made. 0·1579 gram of iodide in 16·8748 grams of chloroform (density of solution $= 1·49$) gave, ten minutes after making up, α_D 0·94° at 16°; hence $[\alpha]_D$ 33·94° and $[M]_D$ 112·1°. This solution likewise became inactive within nine hours of making up.

p-*Bromophenylmethyl*-n-*butylallylammonium Iodide.*

p-*Bromophenylmethyl*-n-*butylallylammonium iodide* was prepared by mixing allyl iodide and *p*-bromophenylmethyl-*n*-butylamine in molecular proportions. The mixture gradually deposited crystals, and, after standing for twenty-four hours, it had completely solidified to a dark red mass. This was dried on a porous plate, and a portion dissolved in alcohol and reprecipitated with ether. It then melted at 84—86°. The melting point gradually rose as this process was repeated, and finally became constant after seven recrystallisations, the value then being 105—106°, and the iodide being obtained in pure white, crystalline needles :

0·1827 gave 0·2732 CO_2 and 0·0878 H_2O. C = 40·78 ; H = 5·33.

$C_{14}H_{21}NBrI$ requires C = 40·96 ; H = 5·17 per cent.

p-*Bromophenylmethyl*-n-*butylallylammonium*-d-*camphorsulphonate* was prepared in the usual manner by boiling molecular quantities of the above iodide and silver *d*-camphorsulphonate with moist ethyl acetate. After the evaporation of the solvent, a clear gum was left. This, on standing in a desiccator, slowly became crystalline, but, although several specimens were prepared both from the crude and from the recrystallised iodide, only in one case was anything like satisfactory crystallisation attained, even when some specimens were kept for months in a vacuum over sulphuric acid. The final product was in each case a white mass, consisting of a small quantity of crystalline matter mixed with a larger quantity of gummy material. All attempts to recrystallise the material failed, although all the usual solvents, alcohol, acetone, ethyl acetate, &c., were used, both alone and as mixtures. Attempts to precipitate the salt from its solutions by adding ether or light petroleum were likewise unsuccessful. In many cases traces of crystals formed, but the amount was too small for investigation, and any attempt to increase the quantity by concentrating the solution led to the immediate deposition of an oil. This is particularly noticeable if ethyl acetate is cautiously added to the solution of the salt in benzene. The crystals deposited in this case were shown to contain no silver, but the quantity was too small for further investigation.

p-*Bromophenylmethyl*-n-*butylallylammonium* d-*bromocamphorsulphonate* was prepared in a similar manner from molecular quantities of the iodide and silver *d*-bromocamphorsulphonate. The behaviour of this substance was completely analogous to that of the camphorsulphonate. It did not crystallise satisfactorily on standing, and if kept for long in a vacuum over sulphuric acid it evolved objectionable odours and seemed partly to decompose. Also, it was found impossible to recrystallise it by any method, although traces of crystals containing no silver were again obtained in one or two cases. In all the others an oil alone separated.

Since it had been shown by Miss Homer (*Proc. Camb. Phil. Soc.*, 1907, **14**, 196), and by H. O. Jones (*Proc. Camb. Phil. Soc.*, 1907, **14**, 376), that asymmetric nitrogen compounds can be resolved by means of tartaric acid, it was decided to try this method in the present case.

p-*Bromophenylmethyl*-n-*butylallylammonium hydrogen* d-*tartrate* was therefore prepared as follows. The iodide was treated in alcoholic solution with a slight excess of silver oxide, and the whole warmed and stirred. The filtrate was allowed to run into an alcoholic solution containing the molecular quantity of *d*-tartaric acid. Instead of evaporating the mixture as far as possible and then waiting for the tartrate to crystallise, the liquid was merely concentrated until it showed signs of cloudiness. A little alcohol was added until the liquid was again clear, and then ether was added until it became just turbid. The tartrate rapidly crystallised on standing, and was recrystallised very easily from alcohol and ether. After four such recrystallisations, a determination of the rotatory power was made:

0·1938 gram in 16·0582 grams of water at 15° gave $\alpha + 0·58°$, whence $[\alpha]_D$ 24·03° and $[M]_D$ 103·68°.

Taking $[M]_D$ for the ion $C_4H_4O_6H$ as 42°, from the results of Landolt on ammonium hydrogen tartrate, it is evident that the salt was resolving rapidly. Accordingly, recrystallisation by the above method was continued, the value for $[M_D]$ gradually increasing and becoming constant after eleven recrystallisations.

The salt was finally obtained in clusters of very small needles, readily soluble in water or alcohol, but only sparingly so in acetone. It melts at about 115° to a cloudy liquid, which effervesces at 141° and becomes clear. For analysis, the salt was dried over sulphuric acid in a desiccator:

0·1906 gave 0·3340 CO_2 and 0·1095 H_2O. C = 47·8; H = 6·38.

$C_{18}H_{26}O_6NBr$ requires C = 49·96; H = 6·07.

$C_{18}H_{26}O_6NBr,H_2O$ requires C = 47·97; H = 6·28 per cent.

An attempt was made to estimate the percentage of water by heating the salt to 105°. The weight, however, decreased slowly, and the decrease continued indefinitely, showing that the tartrate decomposes at this temperature. A precisely similar case of a tartrate retaining water of crystallisation in alcoholic solution has been described by Jones and Hill (Trans., 1908, **93**, 298).

The following determinations of rotatory power were made: After eleven recrystallisations, 0·2126 gram in 15·5070 grams of water at 16° gave α_D 0·86°, whence $[\alpha]_D$ 31·36° and $[M]_D$ 141·1°.

After fourteen recrystallisations, 0·2599 gram in 16·5416 grams of water at 15° gave α_D 0·98, whence $[\alpha]_D$ 31·19° and $[M]_D$ 140·4°

0·2328 gram in 15·7693 grams of water gave α_D – 0·92° at 15°, whence $[\alpha]_D$ 31·49 and $[M]_D$ 141·7°

The mean value is accordingly 141·1° at 15°.

$[M]_D$ above is calculated for $C_{18}H_{26}O_6NBr,H_2O$, which corresponds with $[M]_D$ for $C_{18}H_{26}O_6NBr$.

Taking $[M]_D$ for the ion $C_4H_4O_6H$ as 42°, from the results of Landolt on ammonium hydrogen tartrate, we get $[M]_D$ for the basic ion $C_6H_4Br{\cdot}CH_3{\cdot}C_4H_9{\cdot}C_3H_5{\cdot}N-$ as 98°.

The effect of temperature change on the rotatory power of the solution of the tartrate was next investigated, and proved to be but small. The solution used contained 0·2303 gram of tartrate in 15·1839 grams of water. The values for the acidic ion at different temperatures are those given by Landolt:

t.	α_D.	$[\alpha]_D$.	$[M]_D$.	$[M]_D$ for basic ion.
2°	0·94°	30·98°	139·4°	98·6°
12	0·925	30·48	137·2	95·8
20	0·91	29·99	135·0	94·25
30	0·89	29·33	132·0	89·7
42	0·87	28·68	129·1	86·1
50	0·86	28·34	127·5	84·0

The value of $[M]_D$ for the salt is, of course, $[M]_D$ for the whole molecule, including the water of crystallisation.

p-*Bromophenylmethyl*-n-*butylallylammonium iodide* was slowly precipitated in clusters of needles of some size when the solutions of the above tartrate were rendered faintly alkaline with sodium carbonate solution and then treated with solid potassium iodide.

Determination of its rotatory power in alcohol gave the following results:

0·0993 gram in 9·1716 grams of alcohol (density of solution = 0·809) gave α_D 0·49°, whence $[\alpha]_D$ 27·97° and $[M]_D$ 114·7°.

0·1035 gram in 12·8905 grams of alcohol (density of solution = 0·807) gave α_D 0·36°, whence $[\alpha]_D$ 27·78° and $[M]_D$ 113·9°.

The mean value is accordingly 114·3° at 15°.

The active iodide is but sparingly soluble in chloroform. Determination of its rotatory power in this solvent gave the following results:

0·0786 gram in 16·7587 grams of chloroform (density of solution = 1·492) gave a_D 0·62°, whence $[a]_D$ 44·36° and $[M]_D$ 181·9°.

This measurement was taken at 14° twenty minutes after making up the solution. After one hour, a_D 0·59°; after two hours, a_D 0·53°; after four hours, a_D 0·45°; after six hours, a_D 0·37°; after nine hours, a_D 0·25°. At the end of sixteen hours, the solution was inactive.

0·1314 gram in 18·2003 grams of solvent (density of solution = 1·495) gave a_D 0·95°, whence $[a]_D$ 44·01° and $[M]_D$ 180·4°.

This solution likewise became inactive within sixteen hours. By extrapolation from the curve, the value of $[M]_D$ at the instant of making up the solution is 187·9°.

Since it had been shown that weak acids are available for the resolution of nitrogen compounds, it was decided, after the failure with *d*-camphorsulphonic and *d*-bromocamphorsulphonic acids, to try *d*-camphoric acid in this case.

p-*Bromophenylmethyl*-n-*butylallylammonium d-Camphorate.*—An attempt to resolve the iodide by means of this compound was made simultaneously with the above work on the tartrate. The camphorate was prepared by dissolving the iodide in alcohol and treating with a slight excess of moist silver oxide, the whole being warmed and agitated thoroughly. The mixture was then filtered into an alcoholic solution containing the calculated molecular quantity of camphoric acid. The resulting clear solution was evaporated, as far as possible, on the water-bath, a milky liquid containing a little metallic silver being thus obtained. After standing for a few hours, a white, granular solid was deposited in considerable quantity. This was separated from the oily residue and dried on a porous plate. It was crystallised by precipitation from its alcoholic solution by means of ether, when it separated in beautiful silky needles melting at 147—148°:

0·2183 gave 0·4772 CO_2 and 0·1521 H_2O. C = 59·64; H = 7·74.

$C_{24}H_{36}O_4NBr$ requires C = 59·91; H = 7·54 per cent.

The rotatory power continued to decrease, and became constant after eleven recrystallisations: 0·1523 grams in 16·7965 gram of water gave a_D −0·13°, whence $[a]_D$ −7·17° and $[M]_D$ −34·6°. After thirteen recrystallisations, 0·1224 gram in 16·1218 grams of water gave a'_D −0·11°, whence $[a]_D$ −7·24° and $[M]_D$ −34·9°.

0·1973 gram in 15·5198 grams of water gave a_D −0·18°, whence $[a]_D$ −7·08° and $[M]_D$ −34·1°.

The mean value for the camphorate is accordingly 34·5°. The value of the acid camphoric ion $C_{10}H_{14}O_4H-$ has not previously been determined, and accordingly the sodium, potassium, and hydrogen camphorates were prepared by treating a known weight of the acid with an equivalent amount of the base and making up the solution to a known weight. From these figures, the weights of acid camphorate and water present are easily calculated, and hence $[M]_D$ for the salt determined as usual. In the case of the potassium hydrogen camphorate:

1·0437 grams in 110·4835 grams of water gave α_D 0·59°, whence $[\alpha]_D$ 25·93° and $[M]_D$ 61·7°.

1·2116 grams in 113·9712 grams of water gave α_D 0·55°, whence $[\alpha]_D$ 25·87° and $[M]_D$ 61·6°.

In the case of the sodium hydrogen camphorate:

1·0858 gram in 101·1381 grams of water gave α_D 0·59°, whence $[\alpha]_D$ 27·48° and $[M]_D$ 61°.

Hence the mean value for the ion $C_{10}H_{14}O_4H-$ is 61·4° at 15—18°, and consequently the mean value for the basic ion

$$C_6H_4BrN\cdot CH_3\cdot C_4H_9\cdot C_3H_5N-$$

is $-(61{\cdot}1° + 34{\cdot}5°) = -95{\cdot}9°$.

The effect of temperature on the solution of the potassium hydrogen camphorate was examined, but, owing to the small temperature effect and the sparing solubility of the salts, which precluded the use of solutions stronger than the above, the results obtained were of little value, the differences produced over a range of 30° being within the limits of experimental error.

The above result is of some importance, inasmuch as it is the first occasion on which the resolution of one of these substituted ammonium iodides has been accomplished by more than one method. Moreover, it is the first occasion on which camphoric acid has been made use of in this connexion.

p-*Bromophenylbenzylmethyl*-n-*butylammonium Iodide.*

p-*Bromophenylmethyl*-n-*butylamine* was prepared by the interaction of molecular proportions of bromine and methyl-*n*-butylaniline in acetic acid solution. The acetic acid was then evaporated over the water-bath, and the gummy residue treated with aqueous potassium hydroxide. The base separated as a dark heavy oil, and was collected, washed, and dried over solid potassium hydroxide. It was then distilled, the fraction boiling at 177—181°/18—20 mm. being collected separately. The amine was thus obtained as a pale yellow oil. It did not give a crystalline platinichloride when treated with platinum tetrachloride and hydrochloric acid, a few drops of oil alone settling on standing.

p-*Bromophenyldimethyl*-n-*butylammonium iodide* was prepared by mixing molecular proportions of the base and methyl iodide. A yellow solid gradually crystallised, which, after recrystallisation from alcohol and acetone, melted at 155—156°:

0·1723 gave 0·2353 CO_2 and 0·0782 H_2O. C = 37·26; H = 5·05.
$C_{12}H_{19}NBrI$ requires C = 37·49; H = 4·99 per cent.

The bromine in the amine is in the para-position, since, on heating the above iodide in a sealed tube with excess of methyl iodide, *p*-bromophenyltrimethylammonium iodide, melting at 200°, was obtained, the method being that of Hill (*Proc. Camb. Phil. Soc.*, 1907, **14**, 351).

p-*Bromophenylbenzylmethyl*-n-*butylammonium iodide* was prepared by mixing benzyl iodide and *p*-bromophenylmethyl-*n*-butylamine in molecular proportions and allowing to stand. At the end of twenty hours, the mixture had become crystalline and semi-solid. A portion of the dark red mass was dissolved in hot alcohol, and precipitated by the cautious addition of ether. The resulting product was bright yellow, and melted indefinitely between 117° and 121°. After three such recrystallisations, the iodide was obtained as a pure white, crystalline powder, melting at 135—136° if heated rapidly. Further recrystallisation did not affect the melting point:

0·2357 gave 0·4524 CO_2 and 0·1089 H_2O. C = 52·34; H = 5·14.
$C_{18}H_{23}NBrI$ requires C = 52·68; H = 5·08 per cent.

p-*Bromophenylbenzylmethyl*-n-*butylammonium* d-*bromocamphorsulphonate* was prepared in the usual manner by the interaction of molecular proportions of the above iodide and silver *d*-bromocamphorsulphonate. The iodide used in this preparation was not purified by previous recrystallisation. After evaporation of the solvent, a clear dark red gum remained, which did not crystallise on standing for some months. Although several specimens of this substance were prepared, none was ever obtained crystalline, or could be induced to crystallise by any method.

p-*Bromophenylbenzylmethyl*-n-*butylammonium* d-*camphorsulphonate* was therefore prepared similarly by the interaction of the iodide and silver *d*-camphorsulphonate. The various specimens of this substance prepared, showed wide variation in their readiness to crystallise on standing after the solvent had been removed. Some became crystalline in a few minutes, whilst others did not, no matter how treated. The latter slowly changed to green, amorphous, sticky masses with a very unpleasant odour. The purity of the iodide was found greatly to influence the readiness to crystallise. The crystalline specimens of camphorsulphonate, whilst not crystallising from most solvents and mixtures of such, were easily obtained in the crystalline form by solution in a mixture of toluene and a little acetone, with subsequent concentration over sulphuric acid. The crystals so formed were readily recrystallised by solution in hot acetone and subsequent addition of ether. As finally obtained, the salt formed beautiful silvery plates, very sparingly soluble in acetone, and melting, if heated rapidly, at 174—175°:

0·1730 gave 0·3762 CO_2 and 0·1081 H_2O. C = 59·31; H = 6·94.
$C_{28}H_{38}O_4NBrS$ requires C = 59·53; H = 6·80 per cent.

The rotatory power gradually diminished on recrystallising, and became constant after crystallising eight times as above.

After eight recrystallisations, 0·1714 gram in 11·4932 grams of water gave α_D − 1·37° at 15°, whence $[\alpha]_D$ − 45·93° and $[M]_D$ − 259°.

After eleven recrystallisations, 0·1876 gram in 17·0068 grams of water gave α_D − 1·01° at 15°, whence $[\alpha]_D$ − 45·78° and $[M]_D$ − 258·2°.

0·2442 gram in 12·8178 grams of water gave α_D − 1·75° at 15°, whence $[\alpha]_D$ − 45·90° and $[M]_D$ − 258·87°.

Hence the mean value for the camphorsulphonate is − 258·7°, and the mean value for the basic ion − (258·7° + 50·7°) = − 309·4°.

The effect of temperature change on the rotatory power of the solution of the camphorsulphonate was also investigated, and as usual was found to be comparatively small. The solution used in this experiment contained 0·1876 gram of the camphorsulphonate in 17·0068 grams of water.

t.	α_D.	$[\alpha]_D$.	$[M]_D$.	$[M]_D$ for basic ion.
2°	− 1·02°	− 46·28°	− 260·7°	− 308·7°
10	1·01	45·78	258·2	307·7
20	0·99	44·94	253·4	305·0
30	0·97	44·14	248·9	302·5
40	0·95	43·37	244·6	300·2
50	0·93	42·65	240·5	298·1

p-*Bromophenylbenzylmethyl*-n-*butylammonium iodide* was prepared by the addition of a little solid potassium iodide to the aqueous solution of the camphorsulphonate. The iodide rapidly crystallised, and was collected, washed, and dried. It was thus obtained as a pure white solid, melting, if heated rapidly, at 137—138°. Recrystallisation from cold alcohol and ether left this unchanged; a mixture of the active and inactive iodides melted at 134—135°.

Determination of its rotatory power in alcoholic solution gave the following results:

0·1053 gram in 11·1501 grams of alcohol (density of solution = 0·81) gave α_D − 1·18° at 15°, whence $[\alpha]_D$ − 77·13° and $[M]_D$ − 354·8.

0·1172 gram in 13·2110 grams of alcohol (density of solution = 0·799) gave α_D − 1·09° at 14°, whence $[\alpha]_D$ − 76·89° and $[M]_D$ − 353·7°.

Determination of its rotatory power in chloroform solution gave the following results:

0·1145 gram in 17·95 grams of chloroform (density of solution $=1{\cdot}497$) gave α_D $-1{\cdot}92°$ ten minutes after making up, whence $[\alpha]_D$ $-100{\cdot}5°$ and $[M]_D$ $-462{\cdot}3°$; after one hour, α_D $-1{\cdot}32°$; after two hours, α_D $-0{\cdot}99°$; after four hours, α_D $-0{\cdot}51°$; after six hours, α_D $-0{\cdot}29°$; after nine hours the solution was inactive.

A second determination taken within ten minutes of making up the solution gave α_D $-1{\cdot}46°$ for 0·0937 gram in 19·23 grams of chloroform (density of solution $=1{\cdot}495$), whence $[\alpha]_D$ $-1{\cdot}002°$ and $[M]_D$ $-460{\cdot}9°$. This solution also became inactive within nine hours.

By extrapolation from the curve, the value of $[M]_D$ at the instant of making up the solution is 481·5°.

p-*Bromophenylbenzylmethylallylammonium Iodide.*

p-*Bromophenylbenzylmethylamine* was prepared by the interaction of molecular quantities of benzylmethylaniline and bromine in acetic acid solution. The acetic acid was then evaporated over the water-bath, and the base liberated as a dark oil from the gummy residue by the action of aqueous potassium hydroxide. This was washed and separated, but solidified almost immediately. It was accordingly dissolved in ether, and the solution dried over solid potassium hydroxide, the ether being then evaporated and the residue distilled. The fraction passing over at 218—220°/8—9 mm. was collected separately; it was nearly colourless, and crystallised slowly on standing.

The base forms large, prismatic crystals, very soluble in ether, but insoluble in light petroleum. It is moderately soluble in alcohol, and is readily recrystallised from this solvent. The melting point is about 25°:

0·3165 gave 0·707 CO_2 and 0·1420 H_2O. $C=60{\cdot}92$; $H=4{\cdot}99$.
0·2449 „ 0·5465 CO_2 „ 0·1105 H_2O. $C=60{\cdot}86$; $H=5{\cdot}01$.
$C_{14}H_{14}NBr$ requires $C=60{\cdot}83$; $H=5{\cdot}12$ per cent.

The bromine in this amine is in the para-position, since, on heating it with methyl iodide in a sealed tube at 100°, *p*-bromophenyltrimethylammonium iodide, melting at 200°, is produced. The amine does not yield a crystalline platinichloride on treatment with platinum tetrachloride and hydrochloric acid.

p-*Bromophenylbenzylmethylallylammonium iodide* was prepared by mixing allyl iodide and *p*-bromophenylbenzylmethylamine in molecular proportions. On standing, a crystalline solid and a very viscous, dark red liquid formed. It was found impossible to solidify the liquid by any means, and accordingly it was not used in any of the succeeding experiments. The solid form was dried on a porous plate in a vacuum, and a portion was recrystallised from hot alcohol by the cautious addition of ether. After two such recrystallisations, the melting point became constant at 133—134°, the iodide then being obtained in beautiful iridescent laminæ:

0·2103 gave 0·3527 CO_2 and 0·0846 H_2O. C = 45·74; H = 4·51.
$C_{17}H_{19}NBrI$ requires C = 45·94; H = 4·32 per cent.

p-*Bromophenylbenzylmethylallylammonium* d-*bromocamphorsulphonate* was prepared in the usual manner from molecular quantities of the silver salt and the substituted ammonium iodide. After evaporating the excess of solvent, the solid residue slowly became crystalline. It was found to be capable of recrystallisation if ether was very cautiously added to its acetone solution. The product so obtained was inclined to be somewhat indefinite in crystalline structure at first, but, after two or three recrystallisations, this was no longer the case. After five such recrystallisations, it melted at 137—138°, and a determination of its rotatory power gave the following result:

0·1414 gram in 13·2963 grams of water gave α_D 0·91°, whence $[\alpha]_D$ 42·78° and $[M]_D$ 268·2°.

The rotatory power of the bromocamphorsulphonate ion being about 275°, it follows that slight resolution has occurred, the lævo-form of the base separating. This result was confirmed by precipitating the substituted ammonium iodide from the above solution by the addition of solid potassium iodide, when its solution in alcohol was found to be slightly lævorotatory.

p-*Bromophenylbenzylmethylallylammonium* d-*Camphorsulphonate.*—Owing to the slow resolution of the bromocamphorsulphonate, the corresponding camphorsulphonate was prepared in a similar manner by the interaction of silver *d*-camphorsulphonate and the ammonium iodide. The residue, after the excess of solvent had been evaporated, crystallised rapidly. By adding light petroleum to its acetone solution and then slowly absorbing the acetone by means of sulphuric acid, it was easily recrystallised, and, after four repetitions of this process, a determination showed that resolution was effected far more rapidly than in the former case:

0·1489 gram in 13·0188 grams of water at 15° gave α_D $-0·04$, whence $[\alpha_D]$ $-1·735°$ and $[M]_D$ $-9·5°$.

As resolution proceeded the solubility of the camphorsulphonate in acetone rapidly diminished, and a mixture of acetone and ethyl acetate was used as solvent. The use of alcohol instead of ethyl acetate in this connexion seemed to favour the separation of the dextro-form of the base, the value of $[M]_D$ diminishing and becoming markedly positive.

After twenty recrystallisations from the above mixture, the rotatory power became constant, and the salt was obtained in needles melting at 169°:

0·1729 gave 0·3725 CO_2 and 0·0999 H_2O. C = 58·76; H = 6·42.
$C_{27}H_{34}O_4NBrS$ requires C = 59·08; H = 6·26 per cent.

The following determinations of rotatory power were made:

After twenty recrystallisations, 0·1819 gram in 12·231 grams of water at 16° gave α_D −0·76°, whence $[\alpha]_D$ −25·55° and $[M]_D$ −140·01°.

After twenty-three recrystallisations, 0·1324 gram in 13·9716 grams of water at 15° gave α_D −0·49°, whence $[\alpha]_D$ −25·85° and $[M]_D$ −141·65°.

0·1774 gram in 12·7911 grams of water at 15° gave α_D −0·71°, whence $[\alpha]_D$ −25·59° and $[M]_D$ −140·2°.

Hence the mean value for the basic ion at 15° is −(140·6° + 50 6°) = −191·13°.

The effect of change of temperature on the rotatory power of the solution of the camphorsulphonate was next investigated, with the following results. The solution used contained 0·1791 gram of salt in 16·9945 grams of water:

t.	α_D.	$[\alpha]_D$.	$[M]_D$.	$[M]_D$ for basic ion.
2°	−0·56°	−26·48°	−145·1°	−193·1°
10	0·55	26·01	142·5	192·0
18	0·53	25·08	137·4	189 0
31	0·50	23·73	130·0	183·6
40	0·49	23·34	127·9	183·5
50	0·47	22·49	123·2	180·8

p-*Bromophenylbenzylmethylallylammonium iodide* was slowly precipitated from the aqueous solution of the camphorsulphonate by the addition of solid potassium iodide. The crystals separating were washed and dried, and then melted at 134—135°. Recrystallisation from cold alcohol did not alter this, and a mixture of the active and inactive iodides melted at 134°. Determinations of its rotatory power were made in alcohol and in chloroform solutions:

0·1246 gram in 10·4191 grams of alcohol at 15° (density of solution = 0·81) gave α_D −1·04°, whence $[\alpha]_D$ −53·68° and $[M]_D$ −240·5°.

0·0991 gram in 10·2236 grams of alcohol at 14° (density of solution = 0·808) gave α_D − 0·86°, whence $[\alpha]_D$ −54·9° and $[M]_D$ −243·7°.

0·0912 gram in 17·3176 grams of chloroform at 15° gave (fifteen minutes after making up) α_D −1·12°, whence $]\alpha]_D$ −71·37° and $[M]_D$ −316·9°; after one hour, α_D −1·56°; after two hours, α_D −1·3°; after three hours, α_D −1·07° after four hours, α_D −0·95°;

after six hours α_D $-0{\cdot}78°$; after nine hours, α_D $-0{\cdot}55°$. At the expiration of twenty-four hours the solution was quite inactive.

0·1424 gram in 16·8102 grams of chloroform at 15° (density of solution = 1·496) gave α_D $-1{\cdot}81°$ ten minutes after making up solution; hence $[\alpha]_D$ $-72°$ and $[M]_D$ $-319{\cdot}7°$. This solution was also quite inactive after standing for twenty-four hours. By extrapolation from the curve, the value of $[M]_D$ at the instant of making up the solution was $-346°$.

The results obtained are summarised in the following table:

M. p. of active iodide.	M. p. of *d*-camphor-sulphonate.	M. p. of *d*-bromo-camphor-sulphonate.	$[M]_D$ of ion at 15°.	$[M]_D$ of iodide in alcohol.	$[M]_D$ of iodide in chloroform.	Time required for complete racemisation of chloroform solution.
$PhMe(C_4H_9)(C_3H_5)NI$:						
80°	—	149—150°	85·6°	105·1°	123·0°	9 hours
$C_6H_4Br{\cdot}Me(C_4H_9)(C_3H_5)NI$:						
126	—	—	98·0	114·3	187·9	16 ,,
$C_6H_4Br{\cdot}Me(C_4H_9)(C_7H_7)NI$:						
137	174—175°	—	−309·4	−354·2	−481·5	9 ,,
$C_6H_4Br{\cdot}Me(C_3H_5)(C_7H_7)NI$:						
134—135	169	137—138	−191·1	−242·1	−346·0	24 ,,

In all cases previously recorded, the value of $[M]_D$ for the iodide is greater in chloroform than in alcohol solution, and the former solution soon becomes inactive, owing to racemisation. This relation holds for the above compounds also. The value of $[M]_D$ for the iodide in alcohol is in each case greater than that of the basic ion in water; again a relation to which practically no exception is known.

The influence of temperature on the rotatory power of the ion in aqueous solution is uniform and of the usual linear type, the diagrams obtained being in every way similar to those previously published (*loc. cit.*). As usual, the effect is comparatively slight, being greatest by far in the case of the allyl member of the brominated series, where it is about 15 per cent. The melting point of the resolved iodide and of the inactive compound were in each case practically identical, and both compounds showed the usual property of melting at a temperature appreciably below their true melting point if heated slowly.

The following table brings out the chief relationships observed between the values of $[M]_D$ for the ions containing the groups mentioned:

	n-Butyl.		*iso*Butyl.	
	Allyl.	Benzyl.	Allyl.	Benzyl.
Phenylmethyl	85·6°	253·0° (Wedekind)	55° (Thomas and Jones)	323° (Thomas and Jones)
p-Bromophenylmethyl ...	98·0	309·4	96 (Thomas and Jones)	—

Phenylbenzylmethylallyl	166° (Pope and Peachey)
p-Bromophenylbenzylmethylallyl ...	191·1

It will be seen from this that the relation found in the allyl series by Jones and Hill (Trans., 1908, **93**, 295 *et seq.*), that the brominated compound has a higher molecular rotatory power than the corresponding unbrominated compound, holds good in all the above cases. In the case of the corresponding *n*-butyl and *iso*butyl compounds, no general relation is shown. In one of the above cases, the values are nearly identical, whilst in the remaining two cases they differ widely.

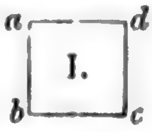
The compounds described in this paper show, however, one marked difference from the majority of those previously examined. It has been stated above that the solution of the active iodide in chloroform rapidly becomes inactive owing to racemisation. The time required for complete loss of optical activity is usually, at least, thirty-six to forty-eight hours, and sometimes considerably more. The *n*-butyl compounds require far less time than this, as will be seen from the table. Only one case of similar rapidity has been previously noted, namely, *l*-phenylbenzylmethyl*iso*butylammonium iodide, which requires only seven hours. The *p*-bromophenylbenzylmethylallylammonium iodide is also more rapid than usual, requiring only twenty-four hours for complete racemisation.

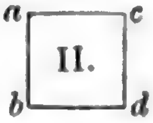
The relation between the values of the molecular rotatory powers of the ions and the values of the product of asymmetry for the asymmetric nitrogen atom or ion may now be discussed.

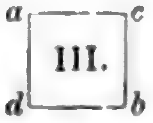
The formula for the product of asymmetry, p'', in terms of the molecular weights or "masses" of the four alkyl groups a, b, c, d producing asymmetry has been shown (Thomas and Jones, *loc. cit.*, 308) to be:

$$p''=\frac{\{(a+d)-(b+c)\}\{(a+b)-(c+d)\}(a-c)(b-d)}{(a+b+c+d)^4},$$

whilst it has been pointed out that there are three possible values of p'', corresponding to the three possible configurations:







In the case of the phenylmethyl-*n*-butylallylammonium iodide, the values are as below, those of the corresponding *iso*butyl and *n*-propyl compounds being appended for purposes of comparison. The values are those given by Thomas and Jones (*loc. cit.*):

Phenylmethylallyl Series: $a = C_6H_5(77)$, $b = CH_3(15)$, $c = C_7H_7(91)$.

	$[M]_D$ for basic ion.	I. $p'' \times 10^3$.	II. $p'' \times 10^3$.	III. $p'' \times 10^3$.
n-Butyl	85·6°	+0·54°	+0·11°	+2·73°
n-Propyl	106·5	−0·59	−0·44	−0·5
*iso*Butyl...............	55·0	+0·54	+0·11	+2·73

To the *p*-bromophenylmethylallyl series (Trans., 1908, **93**, 308) the *n*-butyl and benzyl members have been added:

$a = C_6H_4Br(156)$, $b = CH_3(15)$, $c = C_3H_5(41)$.

	$[M]_D$ for basic ion.	I. $p'' \times 10^3$.	II. $p'' \times 10^3$.	III. $p'' \times 10^3$.
n-Butyl	98°	−10·59	−4·49	+8·46
*iso*Butyl....	96			
n-Propyl..................	141	+9·48	+8·4	+1·3

The benzyl member may, however, be more appropriately compared with the values of Pope and Peachey's similar, but unbrominated, analogue (Trans., 1899, **75**, 1127):

$a = C_6H_5$ or C_6H_4Br, $b = CH_3$, $c = C_3H_5$, $d = C_7H_7$.

	$[M]_D$ for basic ion.	I. $p'' \times 10^3$.	II. $p'' \times 10^3$.	III. $p'' \times 10^3$.
Brominated	191·1°	−7·73	−0·71	+14·6
Unbrominated	167·0	−0·07	+4·87	−1·66

In the case of *p*-bromophenylmethyl-*n*-butylallylammonium iodide, the only available comparison is with Wedekind's similar, but unbrominated, compound:

$a = C_6H_4Br$ or C_6H_5, $b = CH_3$, $c = C_3H_5$, $d = C_4H_9$.

	$[M]_D$ for basic ion.	I. $p'' \times 10^3$.	II. $p'' \times 10^3$.	III. $p'' \times 10^3$.
Brominated	309·4°	−2·92	+8·67	−0·66
Unbrominated	253·0	−0·26	+2·46	−1·71

A glance at the above figures suffices to show that there is no simple relation between the values of p'' and $[M]_D$ for the ion. By no arbitrary assumption as to the configuration to be assigned to given compounds can this difficulty be overcome. The only approach to regularity lies in the last two tables above, where the value of $[M]_D$ for the ion is greater for the brominated than for the unbrominated compound, whilst the value of p'' is also greater if we assign to both compounds configuration I or III in the first table and I or II in the second table.

The almost identical values of the *n*- and *iso*-butyl compounds of the *p*-bromophenylmethylallyl series is worthy of note. A similar case is found in the *n*- and *iso*-propyl compounds of the corresponding unbrominated series.

The writer desires to express his thanks to Mr. H. O. Jones for his kind interest and advice throughout this investigation.

The expenses of this work have been defrayed by grants kindly made by the Government Grant Committee of the Royal Society, for which the author is glad to make this grateful acknowledgment.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

CXIX.—*Acids as Accelerators in the Acetylation of Amino-groups.*

By ALICE EMILY SMITH and KENNEDY JOSEPH PREVITÉ ORTON.

DI-*o*-SUBSTITUTED anilines are notoriously difficult to monoacetylate by means of acetic anhydride if the two ortho-placed atoms or groups are of negative character. Remmers (*Ber.*, 1874, **7**, 350), who investigated systematically the effect of the constitution of the aniline on the rapidity and readiness of acetylation, ascertained that of negative substituents the nitro-group more effectually prevents acetylation than the halogens. Boiling or heating these anilines under pressure with acetic anhydride leads to the formation of a di-, but not of a mono-acetyl derivative (Remmers, *loc. cit.*; Ulffers and von Janson, *Ber.*, 1894, **27**, 93; Sudborough, Trans., 1901, **79**, 532; Orton, Trans., 1902, **81**, 495).

The rapid formation of the diacetyl derivative cannot, as has been suggested, be regarded as due to the direct action of the anhydride on the aniline, thus:

$$\mathrm{Ar{\cdot}NH_2 + O{<}^{CO{\cdot}CH_3}_{CO{\cdot}CH_3} = Ar{\cdot}N{<}^{CO{\cdot}CH_3}_{CO{\cdot}CH_3} + H_2O},$$

for the monoacetyl derivative is just as easily converted into the diacetyl compound as the aniline; moreover, in the treatment of the aniline with the anhydride, the monoacetyl derivative can always be recognised in the early stages of the acetylation. Sudborough's view that the readiness of diacetylation is conditioned by the stability of an acetate formed from the monoacetyl derivative and the acetic anhydride is not open to the same objection.

When the di-*o*-substituted aniline has two or more methyl (or alkyl) groups as substituents in the nucleus (xylenes, ψ-cumene, &c.), one of which groups is in juxtaposition to the amino-group, acetylation is normal.

We have made the observation that the acetylation of such di-*o*-substituted anilines (for example, *s*-tribromoaniline) by acetic anhydride is enormously accelerated by strong acids. Hydrochloric, sulphuric, perchloric, and trichloroacetic acids have been used as catalysts. Nitric and chromic acids behave exceptionally, the former producing a nitroaminobenzene (Orton, Trans., 1902, **81**, 490, 860), and the latter acting as an oxidising agent.*

The effect of the acid as an accelerator is made obvious by the following experiment. A solution of one gram of *s*-tribromoaniline in 20 c.c. of acetic anhydride was kept for a fortnight at the ordinary temperature. The solid was then precipitated by addition of warm water; it melted at 119°, the melting point of the pure aniline. A similar solution was treated with two drops of concentrated sulphuric acid (about 1 gram-molecular proportion), the mixture being kept at the ordinary temperature; at the end of ten minutes, it was poured into warm water; the solid which separated melted at 231°, the melting point of *s*-tribromoacetanilide being 232° (corr.).

The acetylation also takes place, but not so rapidly, if the proportion of acetic anhydride is reduced and the mixture diluted with glacial acetic acid.†

Experiment.—One gram of *s*-tribromoaniline was dissolved in a mixture of 40 c.c. of glacial acetic acid and 4·5 c.c. (15 gram-molecular proportions) of acetic anhydride to which 0·16 c.c. (1 gram-molecular proportion) of sulphuric acid (96 per cent.) was added. The mixture was maintained at the ordinary temperature. At the end of ten minutes, 91 per cent., and at the end of twenty minutes 98—99 per cent., of the aniline was found to be acetylated. The composition of the mixture was determined by estimation of the bromine.‡

---

* Since nitric acid and acetic anhydride convert the aniline into a nitroamine, $Ar{\cdot}NH_2 + HO{\cdot}NO_2 = Ar{\cdot}NH{\cdot}NO_2 + H_2O$, it might have been anticipated that anilides of sulphuric, for example, $Ar{\cdot}NH{\cdot}SO_3H$, or of perchloric acid, $Ar{\cdot}NH{\cdot}ClO_3$, would be produced. No indication of the presence of such substances was detected.

† The commercial acetic anhydride (puriss.) was found to contain traces of sulphate and chloride, which were removed by careful distillation. The acetic acid used by us was fractionated, and then melted at 16·1°. Hence it contained 0·3 per cent. of water.

‡ When in a mixture of *s*-tribromoaniline and *s*-tribromoacetanilide both substances are present in considerable proportion, separation is exceedingly difficult to bring about by recrystallisation from the usual solvents. It is possible, however, to extract the anilide from the mixture by addition of 10 per cent. of sodium hydroxide to a suspension of the solid in alcohol. The anilide entirely dissolves, and, if the liquid is sufficiently diluted with water, no aniline remains in solution in the dilute alcohol. If any diacetyl derivative, which is, of course, insoluble in the alkali, be present, it remains mixed with the aniline (compare Orton, Trans., 1902, **81**, 495.)

Inasmuch as acetic anhydride is without action on *s*-tribromoaniline at the ordinary temperature and yet at the boiling point converts the aniline into the diacetyl derivative, trials have been made with acetic anhydride at temperatures varying between 70° and 100°, and with mixtures of acetic acid and anhydride at these temperatures and at their boiling point. In all cases, a slow acetylation took place.

Experiment.—(1) A solution of 1 gram of the aniline in 20 c.c. of the anhydride was heated at 75°; after two hours, the product contained 25 to 30 per cent. of anilide. More prolonged heating showed that conversion of the mono- into the di-acetyl derivative followed hard on the formation of the former; the melting point of the product rose to a maximum at 192° in three hours, and then gradually fell until the melting point of the pure diacetyl derivative (125°) was reached (see p. 1246).

(2) A solution of 1 gram of the aniline in a mixture of 15 c.c. of acetic anhydride and 20 c.c. of acetic acid was boiled in a reflux apparatus. After six and a-half hours, some 50 per cent. of the aniline was converted into the monoacetyl derivative; after forty-eight hours, the transformation was complete; after ninety-six hours' boiling, no further change, namely, that of the mono- into the di-acetyl derivative, was detected.

Other anilines with like substituents, for example, 2 : 6-dibromo-4-nitro- and 2 : 4-dibromo-6-nitro-anilines, behave generally in the same way as 2 : 4 : 6-tribromoaniline. They are not only acetylated by acetic anhydride extremely slowly at 100°, but are converted in some cases with even greater readiness than the *s*-tribromoaniline into diacetyl derivatives when boiled with this reagent. In the presence of mineral acids, they form monoacetyl derivatives with great rapidity.

The result is very different when anilines of other constitution are treated in the manner described in the foregoing. The acetylation of an aniline in which only one ortho-position is occupied by a negative group is an extremely rapid process. When, for example, a solution of 0·5 gram of 2 : 4-dibromoaniline in 45 c.c. of glacial acetic acid to which 1·25 c.c. ($6\frac{1}{4}$ gram-molecular proportions) of acetic anhydride was added, was kept for five minutes at the ordinary temperature and then poured into boiling water, a quantitative yield of the corresponding anilide (m. p. 144°) was obtained. The addition of mineral acid depresses the speed of acetylation.

Thus, on addition of 2-gram-molecular proportions of hydrochloric acid to the mixture, the presence of the anilide in the product can only just be detected (by fractional precipitation of the solution by water) at the end of five minutes; in an hour, however, acetylation was complete.

A series of experiments on the acetylation of aniline demonstrate the inhibiting effect of acid on the speed of acetylation.

	Aniline.	Glacial acetic acid.	Acetic anhydride.	Sulphuric acid.	Anilide.	Percentage of aniline acetylated.
A.	1 gram	20 c.c.	10 c.c. (9 gr.-mol.)	0	1·34 gr.	92
B.	,,	,,	,,	1 gr.-mol.	1·25 ,,	85·7
C.	,,	,,	3·3 c.c. (3 gr.-mol.)	0	1·29 ,,	88·6
D.	,,	,,	,,	1 gr.-mol.	0·43 ,,	29·5

The four mixtures were kept for one and a-half hours at 10°, then poured into 35 c.c. of warm water, and the liquid, which was placed in a shallow glass dish, was evaporated at the ordinary temperature by drawing rapidly over it a current of air. The anilide, which separated in large crystals, was collected and weighed. In experiment *A*, the acetylation of the aniline, which was shown in other experiments to be complete in a few minutes, was probably quantitative, the solubility of the anilide in the dilute acetic acid accounting for the deficiency of 8 per cent. A comparison of *A* with *B*, and *C* with *D*, brings out very clearly the reduction of the rate of acetylation by the mineral acid.

Effect of the Nature of the Acid.—In testing the effect of acids other than sulphuric, difficulties arise, on the one hand, owing to the low solubility of the acid in the acetic acid or anhydride, and, on the other, in the preparation of the acids in a highly concentrated form. Nitric and chromic acids, which offer less difficulty in these respects, behave, as previously stated, exceptionally; the acceleration of acetylation is masked by other reactions, although traces of the acetyl derivative can be detected with each acid.

We have been able, however, to demonstrate satisfactorily the accelerating effect of hydrochloric, perchloric, and trichloroacetic acids.

A solution of 0·5 gram of *s*-tribromoaniline in 10 c.c. of acetic anhydride to which was added 0·15 c.c. of a 37 per cent. solution of hydrochloric acid (1 gram-molecular proportion) was kept for one and a-half hours, and then poured into warm water. *s*-Tribromoacetanilide, which separated, melted at 227—229°, instead of at 232°. As hydrochloric acid is all but insoluble in acetic anhydride, the concentration of the acid, owing to its obvious escape from the solution, must have fallen below the initial value.

Experiments carried out in acetic acid solution, in which hydrochloric acid is somewhat more soluble, led to a similar result. The aniline and anhydride were in the molecular ratio of 1 : 15, 2 gram-molecules of the hydrochloric acid being present.

Perchloric acid was used in the form of a 5*N*-solution. In one experiment, one gram of *s*-tribromoaniline dissolved in 38 c.c. of acetic acid (98 per cent.) was treated with 5·45 c.c. (18·2 gram-molecular proportions) of acetic anhydride and 0·6 c.c. (1 gram-molecular proportion) of $5N$ (50·25 per cent.) perchloric acid. The mixture was kept for half an hour at the ordinary temperature, and then poured into warm water. The solid material thus obtained, which was a mixture of *s*-tribromo-aniline and -acetanilide, contained 50 per cent. of the latter.

Trichloroacetic acid accelerated the acetylation, but in a far less pronounced manner than the other acids which were tested. In an experiment similar to that just described, only 20 per cent. of the anilide was produced after twenty hours at the ordinary temperature.

Formation of Diacetylanilides.

The formation of diacetyl derivatives is aided by the presence of an acid, but in nothing like the same degree as that of the monoacetyl derivatives.

A solution of 0·2 gram of *s*-tribromoaniline in 20 c.c. of acetic anhydride, to which 0·25 gram-molecular proportion of sulphuric acid was added, contained only the monoacetyl derivative after ten minutes. After remaining for three hours at the ordinary temperature, the formation of the diacetanilide was distinctly shown by the depression of the melting point from 231° (the melting point of the monoacetyl derivative) to 192—213°, but only after forty-eight hours was the diacetylation complete.

If, on the other hand, this mixture, containing the monoacetyl derivative and the sulphuric acid, was maintained at 70—80°, instead of at the ordinary temperature, a quantitative conversion into the diacetyl derivative was brought about in one hour. That the elevation of temperature alone is not the cause of this rapid production of the diacetyl derivative is shown by the fact that only after seven hours' heating of a solution of the monoacetanilide in acetic anhydride at 70—80° is some 70 per cent. of the diacetanilide formed.

At the ordinary temperature, no change was detected in a solution of the acetanilide in acetic anhydride after a long period. The mixture of acetic anhydride and acetic acid used by us (p. 1249), as the experiments described in the foregoing demonstrate, will not carry the acetylation further than the formation of the monoacetyl derivative.

The speed of diacetylation is markedly dependent on the constitution of the aniline. For example, when a nitro-group replaces the para-placed bromine atom, as in 2 : 6-dibromo-4-nitroaniline, monoacetylation in acetic anhydride solution is complete in five minutes in the presence of a quarter or even one-thirteenth gram-molecular proportion of sulphuric acid. This is all the more remarkable, as the solubility of this aniline is such that on using 20 c.c. of anhydride for 0·5 gram of aniline, the major part of the base remains in suspension. If the aniline is sufficiently finely divided, it dissolves very rapidly, the anilide partly separating. When the larger proportion of sulphuric acid is used, the formation of the diacetyl derivative follows quickly on that of the monoacetyl compound. In half an hour, the melting point of the solid product falls far below that of the acetanilide, and after two hours is that of the pure diacetyl derivative.

Acetylation of Phenols.

According to Skraup (*Monatsh.*, 1898, **19**, 458), the acceleration of acetylation of hydroxy-groups by sulphuric acid appears to have been first observed and put into practice in the acetylation of cellulose, &c., by Franchimont (*Compt. rend.*, 1879, **89**, 711). This chemist used the acid as an alternative to zinc chloride and similar reagents, and seemed to regard it as a dehydrating agent. This view, however, is untenable in the light of Skraup's results. The latter ascertained that mere traces of sulphuric acid had a very powerful effect on the acetylation of various hydroxy-compounds by acetic anhydride. Later, Freyss (*Bull. Soc. Ind. Mulhouse*, 1899, 44) tested the use of sulphuric acid in the acetylation of phenols, aldehydes, and aminophenols, &c. Thiele's preparation (*Ber.*, 1898, **31**, 1249) of acetyl derivatives of quinols by treatment of the corresponding quinones with acetic anhydride and sulphuric acid can scarcely be regarded as a reaction of the same type.

To test the effect of different acids, we have chosen *s*-tribromophenol, which yields an acetyl derivative (m. p. 82°), easily isolated and weighed. In the presence of 0·25 gram-molecular proportion of sulphuric acid, a solution of the phenol in a mixture of acetic acid and acetic anhydride (50 per cent.), kept at the ordinary temperature, contains only acetate after half an hour. On replacing the sulphuric acid by perchloric acid, acetylation is equally rapid. In the absence of acid, the phenol is unchanged after twenty-four hours. Nitric acid reacts with the phenol, bromine being eliminated, whilst hydrochloric and trichloroacetic acids scarcely produce an appreciable effect.

Part Played by the Acid.

In our experiments, we have demonstrated that many acids, not only sulphuric acid, are accelerators of acetylation.* For this effect to appear in the case of amines, our results show it to be essential that the amino-group should possess very little power of combining with acids to form ammonium salts. The speed of acetylation of the more basic anilines is lowered, not raised, by acids. When the amino-group is between two ortho-placed (negative) groups, its combining power with acids is, as is well known, greatly reduced, partly possibly on account of the negative character of these groups, and partly by virtue of a steric effect. Moreover, such an amino-group reacts very tardily with acetylating agents, such as acetic anhydride or acetyl chloride. Hence the specific accelerating action of the acid has an opportunity of making itself felt, and is no longer masked either by the conversion of the amino-group into the ammonium compound, which at the same time removes the acid, or by the too rapid action of the amino-group with the acetic anhydride.

---

* In D.R.-P. 147033, a method of acetylating phenylglycine-*o*-carboxylic acid by saturating a solution in acetic anhydride with dry hydrogen chloride is described. The reaction appears to be ascribed to the formation of acetyl chloride.

It is not easy at present to state with precision what is the part played by the acid. Thiele and Winter (*Annalen*, 1900, **311**, 341) are of the opinion that in the acetylation of hydroxy-groups, an anhydride of sulphuric acid and acetic acid, $CH_3\cdot CO\cdot O\cdot SO_3H$, is first formed, which then reacts with the hydroxy-group. This substance was thought by Franchimont to be present in solutions of sulphuric acid in acetic anhydride, and to become converted into a sulphonic derivative of acetic acid, which he isolated.

The peculiar behaviour of nitric acid may be accounted for in this way. The anhydride formed thus:

$$\begin{matrix}CH_3\cdot CO\\ CH_3\cdot CO\end{matrix}\!>O + HO\cdot NO_2 = CH_3\cdot CO_2\cdot NO_2 + CH_3\cdot CO_2H$$

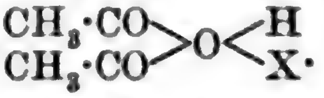
might react with the aniline according to one of the equations:

$$Ar\cdot NH_2 + CH_3\cdot CO_2\cdot NO_2 = Ar\cdot NH\cdot NO_2 + CH_3\cdot CO_2H$$

or

$$Ar\cdot NH_2 + CH_3\cdot CO_2\cdot NO_2 = Ar\cdot NH\cdot CO\cdot CH_3 + HNO_3.$$

As a fact, the acetanilide forms a very small fraction of the product, whereas in the case of sulphuric acid the reaction is mainly, if not entirely, $Ar\cdot NH_2 + CH_3\cdot CO_2\cdot SO_3H = Ar\cdot NH\cdot CO\cdot CH_3 + H_2SO_4$. The feeble effect of hydrochloric acid may also be due to a reluctance to form an anhydride, which is in this case acetyl chloride.

If the cause of the acceleration is to be found in a union of the acid and anhydride, it may be suggested that the complex is not a definite anhydride, but rather of the nature of an oxonium salt,  $\begin{matrix}CH_3\cdot CO\\ CH_3\cdot CO\end{matrix}\!>O<\!\begin{matrix}H\\ X\end{matrix}$.

On such a view less difference would be expected between the various acids than on the hypothesis that the formation of an anhydride is the first step.

The presence of an acid has another effect, which probably plays an important part when the acetylation is carried out in acetic acid solution, that is, in greatly accelerating the interaction of water and the anhydride. In this way, the small quantities of water present in the acetic acid, or in the acid added as catalyst, are removed, and hence the reverse reaction, the hydrolysis of the anilide, is rendered impossible.

The effect of variation of the proportion of the acid on the rate of acetylation of amines and phenols, and a study of the dynamics of the reaction, are under investigation. The preliminary experiments indicate that the speed of acetylation is proportional to the square of the concentration of the acid, that is, doubling the concentration of the acid quadruples the velocity.

Preparation of the Monoacetyl Derivatives of Di-ortho-substituted Anilines.

Most anilines with two negative groups, such as the halogens and the nitro-group, in the ortho-position with respect to the amino-group can be quantitatively converted into their monoacetyl derivatives by the following procedure.

One gram of the aniline is dissolved in 40 c.c. of glacial acetic acid (98—100 per cent.), or in some cases when the aniline is very insoluble it is suspended in this quantity of solvent. Acetic anhydride is next added to the mixture; we have generally used 15 gram-molecular proportions of acetic anhydride to one gram-molecular proportion of aniline, that is, from about 4—6 c.c. of acetic anhydride for one gram of aniline, according to the molecular weight of the aniline. 0·08 c.c. (about four drops) of concentrated sulphuric acid is then introduced, and the mixture kept at the ordinary temperature for forty minutes to an hour. It is then poured into 100 c.c. of warm water, whereupon the anilide immediately separates. Increase of the acetic anhydride hastens the acetylation, but there is danger in some cases, if too large an excess of acetic anhydride is present, of the production of the diacetyl derivative.

We have found this method well adapted to the preparation of the monoacetyl derivatives of 2 : 4 : 6-tribromoaniline and other similar *s*-trihalogen anilines, for 2 : 6-dichloro- and 2 : 6-dibromo-4-nitroanilines, for 2 : 4-dichloro-6-nitroaniline, and for 3-bromo-5-nitro-*p*-toluidine.

2 : 6-Dibromoaniline appears to be somewhat exceptional, and is acetylated only if the proportion of anhydride is considerably higher than that given above. We have prepared the monoacetyl derivative by dissolving the aniline in acetic anhydride and adding the usual proportion of sulphuric acid. The acetylation was complete in two hours.

Preparation of Diacetyl Derivatives.

The di-*o*-substituted anilines just mentioned all form diacetyl derivatives with ease in the presence of mineral acid when the mixture of aniline and acetic anhydride is not diluted with acetic acid, but the rapidity of the reaction depends considerably on the constitution of the aniline. For example, 2 : 6-dibromo-*p*-nitroaniline yields a diacetyl derivative more readily than *s*-tribromoaniline.

s-Tribromodiacetanilide.—This compound can be easily prepared in the following manner: 1 gram of *s*-tribromoaniline is dissolved in 40 c.c. of acetic anhydride to which 0·08 c.c. sulphuric acid ($\frac{1}{2}$ gram-molecular proportion) has been added. The mixture is placed on the water-bath (70—80°) for one hour, and then poured into 100 c.c. of warm water, whereupon the diacetyl derivative crystallises out in the pure state.

2 : 6-*Dichloro-4-nitroacetanilide.* — One gram of the aniline is suspended in 40 c.c. of acetic anhydride to which 0·08 c.c. of sulphuric acid has been added. The aniline passes into solution, the colour disappearing very rapidly. After remaining for two hours at the ordinary temperature, the mixture is poured into warm water. The diacetanilide separates directly in a nearly pure state, melting at 138° instead of 140°.

*The Acetylation of Heptabromo-*p*-hydroxydiphenylamine (s-Tribromophenyl-2′ : 3′ : 5′ : 6′-tetrabromo-4-hydroxyphenylamine).*

In our investigation of the hydroxydiphenylamines (this vol., p. 314), we were unable to prepare the acetyl derivatives by heating the compounds with acetic anhydride and sodium acetate in the ordinary way. We find, however, that the monoacetyl derivatives, in which the acetyl group has replaced the hydrogen of the hydroxy-group, can be very easily obtained when a trace of sulphuric acid is added to the anhydride instead of the sodium acetate.

0·5 Gram of heptabromohydroxydiphenylamine is suspended in 50 c.c. of acetic anhydride to which 0·1 c.c. of sulphuric acid has been added. The mixture is warmed for fifteen minutes on the water-bath, when the compound completely dissolves. On cooling, the *acetate* separates in small, colourless, granular crystals, melting at 193°. The insolubility in warm alcoholic sodium hydroxide showed that the compound no longer contains a hydroxyl group:

0·1212 gave 0·2043 AgBr. Br = 71·74.

$C_{14}H_6O_2NBr_7$ requires Br = 71·78 per cent.

University College of North Wales,
Bangor.

CXX.—*The Hydrolysis of Amygdalin by Emulsin. Part I.*

By S. J. Manson Auld, Ph.D.

Enzymes do not, as a general rule, occur singly, and it is frequently a matter of difficulty to isolate them from the mixture. The influence of these enzymes on one another has not yet been made the subject of much investigation, and it seems within the range of possibility that the presence of other enzymes may have a distinct effect on the action (compare Henry and Auld, *Proc. Roy. Soc.*, 1905, **76**, *B*, 568). It is a matter of concern, therefore, that it has been just those ferments occurring with numerous others that have been employed for the study of enzymic action. Maltase, diastase, zymase, and lipase are all examples of this. It is also the case that many of these enzymes occur in numerous forms, and their source must of necessity be regarded as a factor both in their action and their examination. The maltase of yeast, of malt, and of germinating Indian corn (*Ber.*, 1895, **28**, 1050) are very decidedly different in many respects, and a whole series of diastases is known.

For these reasons it seemed desirable to extend the investigation of enzymic action to emulsin, which, so far as we know, can be readily obtained in a state of "purity," that is, unmixed with other ferments. Further, only three distinct types of emulsin have been described, namely, the ordinary emulsin of sweet and bitter almonds, *Prunus amygdalus var. dulcis* and *Prunus amygdalus var. amara*, the emulsin of *Aspergillus niger*, to which Hérissey (Recherches sur l'Emulsin, *Thèse*, Paris, 1899) ascribes a special action, particularly in the rate of its decomposition of arbutin, and an emulsin associated with phaseolunatin (linamarin) in young flax plants and seeds and in *Phaseolus lunatus* beans. The latter enzyme was stated by Jorissen and Hairs (*Bull. Acad. roy. Belg.*, 1891, **21**, 518) to decompose both amygdalin and linamarin, whilst the emulsin of sweet almonds was without action on the latter. It has been shown, however, that Jorissen and Hairs' emulsin is probably a mixture of ordinary emulsin with a maltase-like ferment, which causes the decomposition of phaseolunatin. It is possible, also, that Hérissey's *aspergillus* emulsin is identical with that of almonds, the evidence to the contrary being rather unsatisfactory.

A third fact renders the investigation of emulsin action necessary and advantageous; on Fischer's system of relating enzyme action to configuration, emulsin is the ferment which alone decomposes the β-glucosides, and in this way is complementary to maltase, which only attacks the α-isomerides.

The hydrolytic action of emulsin has not been the subject of much investigation. One or two old and practically valueless publications exist (compare Marckwort and Hüfner, *J. pr. Chem.*, 1875, [ii], **11**, 202), and the only work of any importance on the subject is that of Tammann (*Zeitsch. physiol. Chem.*, 1892, **16**, 271), who examined the action of emulsin at the same time as that of invertase and diastase. Although generally regarded as a valuable investigation, it contains, even in the small part devoted to emulsin, numerous inaccuracies, some of which will be referred to and discussed later. It must also be remembered that, at the time of the investigation, the law of mass was supposed to govern the course of enzyme action.

It was decided to study the action of emulsin principally with regard to its hydrolysis of amygdalin, the glucoside with which it is chiefly associated in the vegetable kingdom. Amygdalin and emulsin are co-existent, for example, in the seeds of *Prunus amygdalus*, and on macerating these with water the enzyme hydrolyses amygdalin with the production of one molecule each of benzaldehyde and hydrocyanic acid and two molecules of dextrose:

$$C_{20}H_{27}O_{11}N + 2H_2O = C_6H_5{\cdot}CHO + HCN + 2C_6H_{12}O_6.$$

The "Emulsin" of Flax, and the Enzymes of Phaseolus lunatus *and* Manihot utilissima.

As previously mentioned, Jorissen and Hairs isolated a glucoside, linamarin, from germinating flax seeds, which they found to be unacted on by the emulsin of almonds. Co-existent with the glucoside, however, was found an enzyme which, besides hydrolysing linamarin, also decomposes amygdalin and salicin. Up to the present, the general view has been to attribute these different decompositions to the same ferment, and consequently to assume the existence of a special form of emulsin (see Oppenheimer, *Die Fermente*, p. 215). It has lately been shown that the cyanogenetic glucosides of flax, *Linum usitatissimum*, and of sweet and bitter cassava, *Manihot utilissima* and *Manihot aipii*, are identical with phaseolunatin obtained from *Phaseolus lunatus* beans (Dunstan, Henry, and Auld, *Proc. Roy. Soc.*, 1906, **78**, *B*, 145, 152). It was first stated (Dunstan and Henry, *Proc. Roy. Soc.*, 1903, **72**, 285) that phaseolunatin is hydrolysed by emulsin, but it has now been shown that this is not the case, although the enzyme accompanying phaseolunatin also decomposes the naturally-occurring β-glucosides (Dunstan, Henry, and Auld, *Proc. Roy. Soc.*, 1907, **79**, *B*, 315). Similar observations were made with regard to the glucoside and enzyme of cassava. It has been further shown that in decomposing phaseolunatin, the enzymes associated with it in the various plants act as maltase-like ferments, and in similarly decomposing amygdalin, &c., as emulsin-like ferments.

As it was thought that the ferments were probably mixtures, attempts were made to decide the question experimentally. It will be seen by a reference to tables III. and IV. that the hydrolysis of the β-glucosides proceeds much more slowly than that of phaseolunatin. The case is, in fact, almost exactly analogous to that of the maltase contained in extract of malt. It has been shown by Marino and Fiorentino (*Gazzetta*, 1906, **36**, ii, 395) that this enzyme decomposes both α-glucosides, for example, maltase and α-methylglucoside, and β-glucosides, like amygdalin, salicin, &c. This dual action is ascribed to the same enzyme. It is probable that the maltase decomposition may be regarded as the primary action, and the emulsin-like hydrolysis as secondary. As the action of phaseolunatase * might be explained in a similar manner, it was thought advisable to test it from this point of view.

Experiments were first made to determine whether a difference between the optimum temperatures of the actions on amygdalin and phaseolunatin could be observed, but very inconclusive results were obtained, and the attempt was eventually abandoned. The optima of both actions seemed to be between 40° and 50°.

It has been observed, in general, that the maltase ferments are more delicate than emulsin, and particularly more sensitive towards heat when in the dissolved state. Lintner and Kröber (*Ber.*, 1895, **28** 1050) have shown, for example, that yeast maltase is destroyed at 56°, whereas emulsin retains a portion of its activity after being heated for some time at 70° (Henry and Auld, *loc. cit.*). It was thought possible, therefore, that if the action of phaseolunatase is due to two distinct enzymes, they might behave differently towards heat. This has actually been realised experimentally. By carefully heating the enzyme solution and observing the relative rates of decomposition of amygdalin and phaseolunatin, it has been possible to prove that the activity towards the latter glucoside is destroyed before that which causes the decomposition of the β-glucosides. This can readily be seen by reference to table V. In the present state of our knowledge of the enzymes, it is quite justifiable to conclude from these results that phaseolunatase contains two distinct enzymes, and these may be designated the α- and β-enzymes, corresponding with their activity towards α- and β-glucosides. This is preferable to naming them maltase and emulsin respectively, for, although the former enzyme decomposes maltase and α-methylglucoside, the action in both cases is very slow and limited. The highest decompositions of α-methylglucoside were obtained by employing a simple aqueous extract of white (cultivated) *Phaseolus lunatus* beans containing no cyanogenetic glucoside, obtained by macerating the meal with 12 volumes of water mixed with toluene. Fifty c.c. of this solution, added to 10 c.c. of a 3 per cent. solution of the glucoside, and kept at 40° for thirty hours, caused a decomposition of 9·3 per cent.

---

* The term "phaseolunatase" is used to represent the mixtures of enzymes in the three plant species without regard to their dual activity.

The Dynamics of the Hydrolysis of Amygdalin by Emulsin.

The dynamical study of an enzymic hydrolysis differs to a certain extent from that of an ordinary chemical reaction, principally because the products of change eventually exert a decided influence on the character of the hydrolyst. This action being very slight at the commencement of the hydrolysis of amygdalin by emulsin, the measurements of the velocity of reaction have been carried out, as far as possible, over short periods in the initial stages of the reaction.

Influence of the Concentration of Emulsin.—The effect of changing the concentration of emulsin on its action on amygdalin has been studied by Marckwort and Hüfner (*loc. cit.*), who added emulsin dissolved in glycerol to a solution of amygdalin and estimated the amount of glucoside decomposed after fifteen minutes. Their results are, however, practically worthless.

Tammann (*loc. cit.*) has also investigated the effect of increasing the quantity of emulsin in studying its action on salicin. Here, however, he followed the action by means of the polarimeter, and in consequence his results have no absolute value, owing to the fact that the rotatory power of a mixture of salicin and dextrose is not directly proportional to the amount of those substances present in solution. He finds, in accord with the previous workers, that the amount of salicin hydrolysed increases with the concentration of the enzyme, but apparently does not find any definite relationship between the emulsin present and the velocity of reaction.

By measuring only the initial velocities induced by varying quantities of emulsin in separate solutions, and thus avoiding any complications due to secondary action of the decomposition products, it has been found that with small concentrations of the enzyme the velocity of hydrolysis is proportional to the concentration of emulsin. As the concentration is increased this relationship ceases, and eventually a further increase in the quantity of emulsin present produces no corresponding increase in velocity. Taking the formula, $\frac{V_1}{V_2} = \left(\frac{C_1}{C_2}\right)^n$, where V_1 and V_2 are the velocities corresponding with the concentrations C_1 and C_2, the following values of "n" may be calculated from the results given in table VI:

	V_1/V_2.	n.		V_1/V_2.	n.
1.	a/b 0·610	0·96	4.	d/e 0·731	1·23
2.	b/c 0·699	0·96	5.	e/f 0·791	1·32
3.	c/d 0·700	1·02	6.	f/g 0·896	1·36

In the above table, $n = 1$ for moderate concentrations of enzyme, but increases considerably with increase of concentration. This agrees to a certain extent with the observations of E. F. Armstrong (*Proc. Roy. Soc.*, 1904, **73**, 500) on the decomposition of lactose by kefir lactase. Slator (Trans., 1906, **89**, 131) obtained a constant value $n = 1$ for alcoholic fermentation by live yeast, but Herzog (*Zeitsch. physiol. Chem.*, 1902, **37**, 149) with "zymin" (yeast conserved with acetone) found $n = 2$, and Euler (*ibid.*, 1905, **44**, 53) with yeast juice obtained values for n varying from 1·29—1·67.

Influence of the Concentration of Amygdalin.—O'Sullivan and Tompson (Trans., 1890, **57**, 865) studied the course of the reaction of invertase on sucrose, and came to the conclusion that the course of enzymic hydrolysis follows the law of mass action, and that, like the corresponding inversion by acids, it may be expressed by the equation for unimolecular reactions: $\log\frac{C_0}{C_t} = kt$. It was first definitely shown by Adrian Brown (Trans., 1902, **81**, 373) that these conclusions cannot be supported. Working also with invertase, Brown found that the values of k calculated from the above equation gradually increased instead of remaining constant. About the same time, Victor Henri (*Compt. rend.*, 1901, **133**, 891) formulated an empirical law to represent the course of inversion by enzymes, and arrived at the conclusion that the expression $2kt = \log\frac{a + x}{a - x}$ was valid.

In the case of invertase, Adrian Brown and Horace Brown and Glendinning (Trans., 1902, **81**, 388) showed that, when the concentration of the hydrolyte is great compared with that of the enzyme, the decomposition is a linear function of the time, but changes to the logarithmic law in dilute solutions. This has been realised for other enzyme actions by different workers, particularly by E. F. Armstrong (*Proc. Roy. Soc.*, 1904, **73**, 500, 516, 526; **74**, 188, 195) for the sucroclastic enzymes.

It has now been shown that for emulsin, also, the velocity of reaction is independent of the concentration of amygdalin when the latter is present in large excess (table VII). Thus a constant *quantity*, and not a constant *fraction*, of amygdalin is hydrolysed in unit time. Larger quantities of amygdalin begin to produce a retarding effect on the action.

by Google

These results throw no light on the course of hydrolysis when the concentration of the amygdalin is allowed to change owing to the latter being consumed in the reaction, and when outside influences, such as the presence of the products of change, are brought into consideration. If, now, the experiments quoted in table VII are criteria of the velocity of hydrolysis throughout the reaction, the curve obtained by combination of time and hydrolytic activity should be a straight line. This, however, is not the case, for, although the velocity constants calculated from the equation $k = \frac{1}{t}\log\frac{a}{a-x}$ increase continually, the actual velocity decreases very considerably towards the end of the reaction, despite the fact that the hydrolysis does not approach completion. This may be seen from table VIII, which also, from the values of k, proves definitely that the hydrolysis does not follow the law of mass action. In the above expression, a represents the quantity of amygdalin originally present, and x the quantity decomposed after a time t. The non-constancy of the values of k cannot be due to an action in the reverse direction, for this would tend to decrease k, which actually increases during the course of action.

It was shown by Horace Brown and Glendinning (*loc. cit.*) for the diastatic fermentation of starch that the hydrolysis proceeded in two stages. In the first stage at the beginning of the reaction the decomposition was a linear function of the time, but later it actually followed the logarithmic law. The results obtained with emulsin may be interpreted in a similar manner. Up to a decomposition of nearly 50 per cent., equal amounts are hydrolysed in equal times. From this point onwards, D decreases steadily. The results were accordingly recalculated from the ninety minutes' decomposition, and the values of k found corresponding with this time as $t = 0$ and the decomposition as $a = 1$. Some of the numbers obtained are quoted in table X, and from the constancy of the values of k it would appear that the emulsin action also falls into two phases, a linear and a logarithmic, both more or less distinct from each other. The linear phase extends over a very considerable portion of the hydrolysis.

It is worthy of note that, although most of the enzymes have been shown to act apparently independently of the law of mass action, Fokin (*J. Russ. Phys. Chem. Soc.*, 1905, **38**, 858) has quite recently asserted that the action of lipase, obtained, for example, from the seeds of *Chelidonium majus*, proceeds "like other catalytic actions, in accordance with Wilhelmy's logarithmic law." The mass of evidence being against such a view of enzymic action, it seems desirable that Fokin's results should be re-examined and the question of the procedure of lipoclastic action settled.

The fact that the latter part of the hydrolysis of amygdalin by emulsin proceeds according to the logarithmic law, might be explained by supposing that the shape of the curve of the action is merely fortuitous and due to partial destruction of the enzyme. Inhibition of the action by the products of change might also produce a certain constancy in the values of k. It has been proved for invertase by Adrian Brown, however, that where the concentration of enzyme is large compared with that of hydrolyte, the normal course of the hydrolysis obeys the law of mass action. The constancy of the recalculated k values might therefore be explained by assuming that the concentration of amygdalin had become sufficiently small to cause this second stage of the reaction. It was decided therefore to investigate the hydrolysis in dilute amygdalin solutions in the hope that this logarithmic stage would be actually realised.

The great difficulty in such experiments was to obtain a sufficient dilution without causing the reaction to proceed so quickly that it could not be followed quantitatively. Numerous experiments were carried out under varying conditions, and it was eventually found possible to trace the logarithmic phase of the hydrolysis (table X).

The generally accepted explanation of the fact that the velocity of enzyme hydrolysis is independent of the concentration of hydrolyte is the assumption that a compound is produced by interaction of enzyme and substance. If the compound thus formed lasts for an appreciable time, it will follow that, assuming the enzyme to be completely regenerated, alteration of the concentration of hydrolyte will have no effect, and equal amounts of the latter will be decomposed in equal times. Only when the concentration of the substance under examination becomes so small that a quantity of the enzyme remains uncombined will it have any effect on the course of hydrolysis. The results obtained with emulsin and amygdalin are completely in accord with this theory. It follows, for instance, that the quantity of enzyme, being completely combined with the hydrolyte, is a measure of the amount of compound formed, and therefore of the velocity of reaction. An increase in the quantity of enzyme should show a proportional increase in the rate of hydrolysis. This is, of course, actually the case, although other workers have obtained results not so easily explained. Herzog (*loc. cit.*), for instance, showed that the velocity of alcoholic fermentation is proportional to the square of the concentration of zymase. As pointed out by Slator (*loc. cit.*), however, the constancy of k in Herzog's results is probably due to partial decomposition of the enzyme. Fokin's results may possibly be explained in a similar manner, for lipase, as is well known, is a particularly sensitive enzyme.

Retardation of the Hydrolysis.—Enzyme action, in general, is capable of inhibition by a large number of agents, and it has been in the study of the effect of retarding agents that any insight into their structure and action has been obtained.

Inhibition of enzyme hydrolysis may be caused in three ways: (*a*) By destruction of the enzyme; generally by coagulation through the action of substances of acid or basic character, sometimes by salts, and always by heat. (*b*) By combination of the enzyme with substances other than the hydrolyte. (*c*) By reverse action.

In the natural course of hydrolysis, only the last two come into consideration, and (*c*) only to a very small extent.

Retardation Caused by the Products of Reaction.—In the enzyme hydrolyses already studied, it has been shown that the products of reaction are the principal factors in causing the reaction to cease, and that by removal of these products the action will proceed to a finish (Tammann, *loc. cit.*).

The retardation caused by the products of the reaction of the hydrolysis of amygdalin by emulsin, namely, benzaldehyde, hydrocyanic acid, and dextrose, has been investigated by the addition of known quantities of these substances, both alone and together, to the reacting mixture and observing the change in the velocity of reaction. The results obtained are, on the whole, in agreement with some less comprehensive experiments carried out by Tammann in the same direction. Benzaldehyde and hydrocyanic acid have, it would appear, greater retarding effect on the action than dextrose, but here the results differ from those of Tammann, who attributed a stronger inhibiting action to hydrocyanic acid than to benzaldehyde. From tables XI, XII, and XIII this would not seem to be the case, and the values obtained are more in agreement with the views of Jacobson (*Zeitsch. physiol. Chem.*, 1892, **16**, 367) and Marino and Fiorentino (*Gazzetta*, 1906, **36**, ii, 395), who contend that the action of emulsin is not affected by the presence of hydrocyanic acid. This, however, is also only partly correct, as hydrocyanic acid exerts a distinct retarding action.

It is impossible, of course, to draw any relationship between the retardation caused by benzaldehyde, hydrocyanic acid, and dextrose and the fact that they *are* products of reaction. The dextrose probably inhibits in this, as in other cases, by recombination with the enzyme to form complex carbohydrates, and the hydrocyanic acid will retard the action as a weak acid (see later). The behaviour of the benzaldehyde cannot be explained in the same manner. It seems, however, to be, in itself, a "poison" towards enzyme action. As is well known, phenol is generally without action on enzyme activity, and is frequently used for sterilising purposes. Salicylaldehyde, however, at once inhibits enzyme action, and has been used for this purpose in cases where it was necessary to stop the hydrolysis at a certain point (E. F. Armstrong, Trans., 1903, **83**, 1305). To the CHO group therefore must be ascribed "enzymicidic" properties, and benzaldehyde would naturally belong to this class. That this is actually the case may be seen from the following experiment carried out with invertase and sucrose. To two flasks containing 1·5 grams of sucrose dissolved in 15 c.c. of water were added 5 c.c. of a 1 per cent. solution of an invertase preparation, and in one of the flasks was placed three drops of benzaldehyde. After three-quarters of an hour at 31°, the respective amounts of sugar inverted as determined polarimetrically were found to be 51·0 and 39·6 per cent.

Inhibition of the Hydrolysis by Acids and Bases.—The action of acids on the activity of enzymes has been the subject of a considerable amount of investigation, but, unfortunately, the results obtained differ very considerably among themselves, even when obtained under apparently similar conditions. It is thus almost impossible to formulate a general law, and even for specific enzymes an agreement as to the effect of acids has been arrived at only in one or two cases. It can, of course, be said definitely that strong acids destroy enzyme activity, but we are here only concerned with low concentrations.

With regard to emulsin, the only experiments on record are those of Jacobson (*loc. cit.*), who investigated the property of various ferments of destroying hydrogen peroxide catalytically with evolution of oxygen. No quantitative experiments are on record, however, on the specific action of emulsin when influenced by dilute acids. Jacobson's results on the catalytic activity of emulsin are of interest in that they show that hydrochloric acid has no accelerating effect on the action even in dilute solutions.

In studying the "poisonous" effect of acids on the emulsin hydrolysis, dilute solutions of sulphuric, hydrochloric, acetic, and lactic acids were employed. The results obtained are given in tables XVI, XVII, XVIII, and XIX.

The inhibiting effect of alkalis (potassium hydroxide and sodium hydrogen carbonate) has also been investigated, and the results are set forth in tables XX, XXI and XXII.

In its behaviour towards acids and alkalis, emulsin acts in a peculiar manner, distinct from the generally understood behaviour of most of the other unorganised ferments. In the first place, it would appear that the optimum action of emulsin does not lie in acid or alkaline solution, as is the case with the majority of enzymes. True, hydrocyanic acid in very small quantities has a slight accelerating effect on the action, but this increase in activity is not comparable, for example, with the effect of acid solutions on peptic proteolysis. Emulsin seems therefore to possess its optimum activity in neutral solution.

Of far greater importance is the fact elucidated that during their gradual inhibition of the power of emulsic hydrolysis, mineral acids and alkalis only partly destroy the activity, and that a neutralisation by alkalis or acids restores or reactivates the enzyme to a large extent. Senter (*loc. cit.*) has found that the inhibiting action of acids on hæmase is proportional to the concentration of the hydrogen ions, and from his results concludes that the enzyme is a weak base. Here, however, we have distinct primary evidence that emulsin is capable of combining with both acids and bases to form salts, from which it may be recovered in the usual way. The enzyme would thus appear to be at the same time both acid and base, and is in fact amphoteric in character. That neither of the functions is very strong is obvious from the fact that salt formation only takes place to a limited extent with the weaker acids and bases.

The possibility of enzymic salt formation at once raises the question of the nature of enzymes, and especially whether the ferments themselves are material substances, and capable of actual salt formation. Unless this is the case, one must assume that the energy centres of which the enzyme is composed are bound up so intimately with their material substrata that chemical reactions involving the latter produce absolutely corresponding effects on the former. In either case it must be concluded from these experiments that the activity of enzymes is more intimately bound up with the molecule of the protein compounds with which they are invariably associated, than has hitherto been generally supposed. The protein molecule itself is both acid and basic in character, and the addition of small quantities of acids and alkalis consequently causes protein salt formation. If, however, the acid or alkali is present in somewhat higher concentration, the structure of the protein is completely altered and acid-albumins and alkali-albuminates are produced. From these compounds, the protein cannot be regenerated. The connexion with enzyme activity seems obvious: we have first of all with strong acids and alkalis of low concentrations, salt formation in the protein molecule, and a corresponding paralysis of the enzyme. Higher concentrations of hydrogen and hydroxyl ions produce the acid-albumins and alkali-albuminates, and destroy the enzyme activity.

Considering the dependence of the activity of emulsin on the presence of basic and acidic groups, and the fact that the glucosides hydrolysed contain no corresponding groups for attachment, that is, that the compound of enzyme and hydrolyte is probably not of the nature of a salt, it is probable that the catalytic activity is bound up with a combination involving a dynamic change in the enzyme molecule, such as would be expressed, for example, in a cyclic transformation of amino-acid into acid amide. Such a view of the hydrolysis must, however, be reconciled with the fact that emulsin is essentially specific in its action and only decomposes glucosides which contain the β-lactonic grouping in the sugar residue. It is well known, however, that the protein molecule also contains carbohydrate groupings (compare Blumenthal and Mayer, *Ber.*, 1899, **32**, 274), and it is not difficult to imagine combination of enzyme and hydrolyte only taking place when both contain the same or complementary similarly constructed sugar molecules. Such a view would be a literal fulfilment of Fischer's "lock and key" aspect of enzyme hydrolysis.

Extent of the Hydrolysis.—The hydrolysis of amygdalin by emulsin is not complete. This fact was first recognised by Liebig, who believed that the reaction proceeded only so long as the benzaldehyde produced dissolved in the water. This, of course, is not the case. Tammann (*loc. cit.*) also showed that the action is not finished, but his results differ from one another very considerably. Thus, although, in other parts of the paper, decompositions of amygdalin as high as 80 per cent. are implied, in the set of experiments devoted to the effect of increasing the quantity of emulsin at 40° a maximum decomposition of only 60 per cent. is obtained.

Quite recently, and after this research was well advanced, Caldwell and Courtauld (Trans., 1907, **91**, 670) repeated Tammann's experiments, and calculated the amount of change by observation of the rotatory power and by estimation of the benzaldehyde produced. They found that the maximum hydrolysis after sixty-seven and ninety hours amounted to 98·2 and 98·5 per cent. respectively. From estimations of the hydrocyanic acid produced, however, only 86·1 per cent. of the amygdalin appeared to be decomposed. Indeed, lower figures were invariably obtained from the hydrocyanic acid than from the benzaldehyde or rotatory power. No explanation of this deficiency is given, although such a deficiency is apparently to be ascribed to the hydrolysis of all cyanogenetic glucosides.

Employing the method described later for the estimation of hydrocyanic acid, no difficulty was experienced in obtaining much more profound decompositions of amygdalin calculated from a hydrocyanic acid basis than those described either by Tammann or Caldwell and Courtauld. Referring to table VIII, it will be seen that a decomposition of 93·3 per cent. is recorded in only twenty-two hours. In other cases, where the decomposition was measured over twenty-four hours and larger quantities of emulsin used, 97·0 per cent. of the amygdalin was found to be hydrolysed, but this was the maximum decomposition observed. It is suggested that Caldwell and Courtauld's results are somewhat high, as by carefully removing the hydrocyanic acid from alkaline solution with ferrous and ferric hydroxides and then estimating the benzaldehyde by Ripper's method (*Zeitsch. anal. Chem.*, 1902, **41**, 61), values have been obtained agreeing approximately with those from the hydrocyanic acid estimation. In some cases, indeed, they were slightly lower. The results obtained are given in table XXIII.

The Equilibrium, Reversibility.—Although the amount of glucoside remaining undecomposed (say 2 per cent.) falls far short of that claimed by Tammann, it is still sufficient to cause an assumption of equilibrium, an equilibrium which that author claims to be dependent on temperature.

Tammann himself tested the synthetic action of emulsin by placing glucose, hydrocyanic acid, and benzaldehyde on his tongue together with some emulsin, and awaiting the bitter taste of amygdalin. He failed to obtain any indication of reversible action by this means, however, which is scarcely surprising. No further experiments in this direction are on record, although Emmerling (*Ber.*, 1901, **34**, 3810) has succeeded in synthesising amygdalin from mandelonitrile glucoside by the aid of maltase. An extensive series of experiments was therefore set on foot to test the synthetic action of emulsin as an explanation of incompletion of the hydrolysis of amygdalin. The experiments were of two classes, namely, those where the amount of reacting substances present was measured from time to time, and that where an attempt was made after a considerable period to isolate amygdalin Both series were wholly unsuccessful, and no account of the experiments need be given here.

Effect of Temperature on the Hydrolysis.—Temperature has a very marked effect on the velocity of all fermentation processes. The velocity of reaction is generally very small at low temperatures, and gradually increases to a point known as the *optimum* temperature of the ferment, from which point onward it again decreases until the ferment is completely destroyed by the heat action.

Tammann states that the temperature has a great effect on the amount of amygdalin decomposed by emulsin, that is, on the end point of the action, and uses this as a main argument against the incompletion of the process being a chemical equilibrium. His views will apparently not bear investigation, however, as will be seen by contrasting his results with those quoted in table XXIII. The highest decompositions during the hydrolysis of salicin and amygdalin by emulsin were obtained between 45° and 50°, and, as previously mentioned, amounted only to about 80 per cent. At 40°, the end point is stated to be at a 60 per cent. hydrolysis of the amygdalin present. Contrast this, however, with the 93 per cent. and 97 per cent. hydrolyses obtained at the same temperature without any great difficulty, and the erroneous nature of Tammann's statement becomes apparent.

Temperature Coefficients.—The general method of expressing the change in velocity of reaction due to change of temperature is to calculate the ratio of velocities for an interval of 10°. For most reactions, $\frac{k_t + _{10}}{k_t}$ lies between 2 and 3.

For the hydrolysis of amygdalin by emulsin, measurements were made at every 5° from 15° to 60°, and only initial velocities were taken, that is, while the velocity was still a linear time function. The observations were thus absolutely comparable. It will be observed from tables XXIV and XXV that the temperature-coefficient varies with the temperature, and only twice reaches the general value of between 2 and 3. The results are of the same order as those calculated from Tammann's figures for salicin.

Opportunity is taken here for correcting a serious error in this connexion in van't Hoff's "Lectures on Theoretical and Physical Chemistry, Part I." On pages 225 to 235 the velocity of the fermentation of salicin by emulsin is continually referred to as having a temperature-coefficient of 7·14 at from 60—75°. These figures are obtained by calculation from experiments by Tammann (*Zeitsch. physikal. Chem.*, 1895, **18**, 433). This is so obviously erroneous, it having been shown that the velocity of reaction of emulsin hydrolysis is practically nothing at 70° (Henry and Auld, *loc. cit.*), that it is hardly necessary to turn to the original to find that the results refer to the rate of destruction of emulsin activity on heating. This, as is well known, increases with great rapidity with rise of temperature and thus affords a temperature-coefficient of abnormal size.

EXPERIMENTAL.

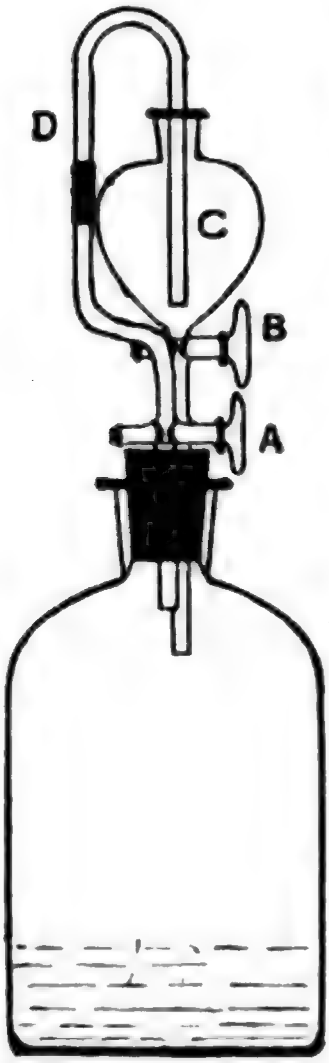
Analytical.—Three chief methods are open for the measurement of the hydrolysis, namely, estimation of the amount of hydrocyanic acid produced, measurement of the amount of dextrose formed, or observation of the change of rotatory power of the liquid. The two last methods are open to serious objection. Estimations of dextrose depending on its power of reducing alkaline copper solutions are difficult to carry out rapidly and accurately, and the fact that the character of the dextrose residues in amygdalin was unknown, made it impossible to follow the reaction by means of the polarimeter. To these objections must be added the possibility of the intermediate formation of a diglucose of unknown reducing and optical rotatory power. Determination of the amount of benzaldehyde formed or of the decrease in the quantity of amygdalin present offering no satisfactory solution of the question, it was decided to follow the hydrolysis by estimating the hydrocyanic acid produced. At first, this was estimated by means of standard silver nitrate solution, but as this process could not be carried out with accuracy in the experimental liquid and consequently necessitated a distillation for each estimation, it was abandoned in favour of the modification of Fordos and Gelis' method (*J. pr. Chem.*, 1852, 59, 255) described by Dunstan and Henry (*Proc. Roy. Soc.*, 1903, 72, 287). This method consists in titrating the liquid containing hydrocyanic acid with a standard iodine solution :

$$HCN + I_2 = CNI + HI.$$

Excess of sodium hydrogen carbonate solution is added to prevent an accumulation of hydriodic acid.

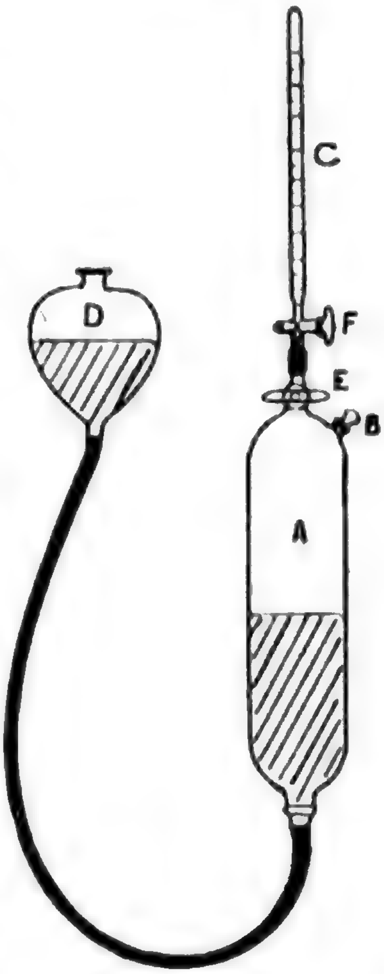
As it was necessary to work at temperatures where a considerable amount of the hydrocyanic acid formed would be in the gaseous state and would otherwise occasion a loss on opening the experimental vessels, special apparatus was devised to prevent any escape of vapour. In most of the experiments a separate vessel was used for each concentration of the reacting substances, and in such cases the small apparatus shown in Fig. 1 was employed. During the course of the reaction, the two taps, *A* and *B*, are kept closed. At the moment the hydrolysis is to be stopped, both taps are opened, and saturated sodium hydrogen carbonate solution flows into the bottle from the funnel *C*. At the same time, any escaping vapour is forced out through the side-tube *D*, and bubbles through the solution in the funnel by which it is carried back into the flask. When most of the bicarbonate solution has been run in, the taps are again closed, the contents shaken, and cooled under the tap. If the tap *A* alone is now opened, the remaining sodium hydrogen carbonate solution is sucked back through the side-tube, and frees it from any hydrogen cyanide remaining. The contents of the flask are then titrated in the ordinary manner, using starch solution as indicator.

FIG. 1.



In those cases in which it was necessary to carry out a series of experiments in the same solution, and abstract aliquot parts for examination at stated intervals, a different arrangement was required, owing to the necessity of keeping all the hydrocyanic acid in the dissolved state. It was found by experiment that a surface of metallic mercury had no inhibiting effect on the action of emulsin on amygdalin, and the arrangement seen in Fig. 2 was consequently employed. The experimental vessel consists of the tube *A*, closed at the top by a tap, *E*, and fitted with a stoppered side-tube, *B*, to facilitate the introduction of the enzyme and hydrolyte. The lower part of the tube is filled with mercury, which can be raised to the desired level by means of the reservoir *D*. The apparatus containing the amygdalin solution having acquired the necessary temperature by immersion in a thermostat, the emulsin is added, and the solutions well mixed. The tap *E* having been opened, *D* is now raised until the liquid just fills the vessel. The tap is now closed, and the whole apparatus immersed in the bath. To remove a stated volume of the liquid for examination, the bulb *D* is raised, and on opening the tap *E* the liquid is forced out into the tapped pipette *C*, which is connected with the tube *A* by a small piece of indiarubber tubing. The liquid is then run out into excess of sodium hydrogen carbonate solution, and the pipette washed out with the same liquid.

FIG. 2.



The sodium hydrogen carbonate thus effects a three-fold purpose. It absorbs the hydrocyanic acid, it is necessary for the iodine titration, and its addition at once stops the action of the emulsin. The accuracy of the last statement is seen at once from the following table:

TABLE I.

For each experiment, 25 c.c. of amygdalin solution (2 per cent.) were mixed with 2 c.c. of emulsin solution (2 per cent.). After twenty minutes, the sodium hydrogen carbonate (normal solution) was added, and the reaction allowed to proceed for another twenty minutes.

Time of action, mins.	$NaHCO_3$ added, c.c.	HCN formed, gram.	Amygdalin decomposed, per cent.
—	—	0·00130	12·7
20	0·25	0·00197	15·1
20	0·5	0·00144	13·4
20	1·0	0·00135	12·8
20	2·0	0·00130	12·7

$T = 38·5°$.

For the hydrocyanic acid titration, it was found that *N*/50 iodine solution gave the best results, but *N*/100 iodine was also used in some cases where only a small decomposition had taken place. When *N*/10 iodine was employed, the results were not constant, but increased considerably on standing. This was probably due to the production of larger quantities of hydrogen iodide than could be absorbed at once by the sodium hydrogen carbonate, and the reaction being reversible, hydrocyanic acid would be regenerated.

Neither amygdalin nor its other decomposition products absorbs iodine, and the enzyme solution does so only after some time. As the complete estimation was usually carried out in one or two minutes, this involved no source of error, and the titration could be carried out in the experimental liquid.

The amygdalin employed was Merck's pure product recrystallised. The emulsin was also obtained from Merck's preparation, and was purified by dissolving in water and reprecipitating the filtered solution with 90 per cent. alcohol. The product obtained in this way dissolved completely in water. All solutions were kept sterile, generally by the addition of a little chloroform.

Phaseolunatase.

As the enzymes of *Phaseolus lunatus*, flax, and cassava all act in the same manner, it generally sufficed to carry out the experiments with one of them only. In most cases the enzyme obtained from Java beans was employed, and all the following experiments were carried out with it.

For the preparation of the enzyme, the beans, roots, or germinating seeds are dried thoroughly in the air, ground to a fine meal, and soaked with three volumes of water mixed with 1 per cent. of toluene, which is added for sterilising purposes. After several hours, the liquid is filtered, and allowed to stand in a vacuum desiccator over sticks of potassium hydroxide until all the hydrocyanic acid has been absorbed. The concentrated liquid is then poured into excess of alcohol, the precipitated enzyme quickly filtered and washed with a little alcohol, after which it is dried in a vacuum and finely powdered. If the substance is not completely redissolved by water, the process of solution and precipitation is again repeated.

The enzymes form fine white powders, capable of being kept in the active state for many months.

TABLE II.

Hydrolysis of Amygdalin by Phaseolunatase.

For each experiment, 10 c.c. of amygdalin solution (1 per cent.) were mixed with 30 c.c. of enzyme solution (2 per cent.):

Time of action, mins.	HCN formed, gram.	Amygdalin decompose, per cent.
60	0·00204	34·5
120	0·00252	42·7
180	0·00301	50·9
240	0·00340	57·6

$T = 40·0°$.

TABLE III.

Hydrolysis of Salicin by Phaseolunatase.

For each experiment, 10 c.c. of salicin solution (2 per cent.) were mixed with 30 c.c. of enzyme solution.

Time of action, mins.	Cu_2O formed, gram.	Glucose produced, gram.	Salicin decomposed, per cent.
—	0·0535	—	—
30	0·0924	0·0199	15·8
60	0·1313	0·0389	30·9
120	0·2019	0·0742	59·0
180	0·2265	0·0865	68·7

$T = 39·5°$.

TABLE IV.

Hydrolysis of Phaseolunatin by Phaseolunatase.

For each experiment, 15 c.c. of phaseolunatin solution (2 per cent.) were employed.

Time of action, mins.	Weight of enzyme, gram.	HCN formed, gram.	Phaseolunatin decomposed, per cent.
30	0·2	0·0106	31·8
60	0·2	0·0206	61·8
30	0·1	0·0055	16·5
60	0·1	0·0104	31·2

$T = 40·0°$.

TABLE V.

Action of Phaseolunatase on Amygdalin and Phaseolunatin after heating between 40° *and* 65°.

For the decomposition of the amygdalin, 20 c.c. of the glucoside were mixed with 10 c.c. of enzyme solution. For the phaseolunatin, 20 c.c. of glucoside (2 per cent.) were mixed with 5 c.c. of enzyme solution.

Temperature to which enzyme solution was heated.	Time of heating, mins.	Decomposition of amygdalin.			Decomposition of phaseolunatin		
		Time of action, mins.	HCN formed, gram.	Amygdalin decomposed, per cent.	Time of action, mins.	HCN formed, gram.	Phaseolunatin decomposed, per cent.
40°	—	60	0·00136	5·8	30	0·00733	16·5
		120	0·00262	11·1	60	0·01413	31·8
45	60	60	0·00128	5·6	30	0·00591	13·3
		120	0·00260	11·0	60		
50	120	60	0·00128	5·6	30	0·00355	8·0
		120	0·00262	11·1			
55	60	60	0·00120	5·1	30	0·00160	3·6
60	60	60	0·00101	4·3	60	—	—
		120	0·00189	8·0	120	0·00049	1·1
65	60	60	0·00042	1·8	60	—	—
					120	—	—

TABLE VI.

Influence of the Concentration of Emulsin on the Velocity of Hydrolysis.

In the following experiments, 50 c.c. of amygdalin solution (2 per cent.) were mixed with a 2 per cent. solution of emulsin.

t = time of action in minutes; A = the percentage of amygdalin decomposed; D = difference in successive readings. The hydrocyanic acid formed is given in grams.

Temp. = 41°.

a. 2 c.c. emulsin.

t.	HCN.	*A.*	*D.*
10	0·00060	3·6	3·6
20	0·00125	7·3	3·7
30	0·00190	11·1	3·8

Mean velocity = 3·7 per cent. per ten minutes.

b. 3 c.c. emulsin.

10	0·00101	6·0	6·0
20	0·00202	12·0	6·0
30	0·00303	18·1	6·1

Mean velocity = 6·05 per cent. per ten minutes.

c. 4 c.c. emulsin.

10	0·00146	8·9	8·9
20	0·00279	17·1	8·2

Mean velocity = 8·7 per cent. per ten minutes.

d. 6 c.c. emulsin.

10	0·00215	12·5	12·5
20	0·00380*	23·2	10·7

Mean velocity = 12·5 per cent. per ten minutes.

e. 12 c.c. emulsin.

5	0·00145	8·6	8·6
10	0·00288	17·1	8·5

Mean velocity = 17·15 per cent. per ten minutes.

f. 25 c.c. emulsin.

10	0·00363	21·6	—

Velocity = 21·6 per cent. per ten minutes.

g. 50 c.c. emulsin.

5	0·00215	12·8	12·8
10	0·00406	24·1	11·3

Velocity = 24·1 per cent. per ten minutes.

---

* This reading showing a great falling off in velocity for the higher decomposition was rejected, and the decomposition for the first ten minutes alone taken.

TABLE VII.

Influence of the Concentration of Amygdalin on the Hydrolysis in Strong Solutions.

For each experiment, 1 c.c. of emulsin solution (2 per cent.) was used, and the decomposition measured over a definite period.

Temp. = 39·5°. Vol. = 50 c.c.

Time of action, mins.	Weight of amygdalin used, grams.	HCN formed, gram.	Amygdalin decomposed, per cent.	Weight of amygdalin decomposed, gram.
20	0·1	0·00274	46·4	0·046
20	0·2	0·00274	23·2	0·046
20	0·3	0·00260	14·7	0·044
20	0·4	0·00260	11·0	0·044
20	0·6	0·00253	7·2	0·043
25	0·8	0·00348	7·4	0·059
25	1·0	0·00348	5·9	0·059
25	1·25	0·00340	4·6	0·058
25	1·5	0·00332	3·7	0·056

TABLE VIII.

Hydrolysis of Amygdalin by Emulsin in One Solution.

Volume of amygdalin solution (2 per cent.) = 300 c.c.
Volume of emulsin solution (2 per cent.) = 15 c.c.

15 c.c. were examined every ten minutes until 150 minutes had elapsed, when 10 c.c. only were taken.

Temp. = 40·0°.

Time of action, mins.	HCN formed, gram.	Amygdalin decomposed, per cent.	Difference per 10 mins.	$0·4343K = 1/t \log a/a-x$.
10	0·00096	6·1	6·1	255×10^{-5}
80	0·00707	45·2	5·4	295×10^{-5}
100	0·00859	54·9	4·8	309×10^{-5}
150	0·00784	75·3	4·6	347×10^{-5}
1360	0·00963	93·3	—	44×10^{-5}

TABLE IX.

Old times, mins.	New times, mins.	$0·4343K = 1/t \log a/a-x$.
110	20	485×10^{-5}
140	50	488×10^{-5}
160	70	491×10^{-5}

Mean of total values (100—180 mins.) = 481×10^{-5}.

Table X.

Hydrolysis of Amygdalin by Emulsin in Dilute Solution.

Volume of (2 per cent.) emulsin solution used = 3 c.c.
Total volume of solution = 20 c.c.

Time of action, mins.	Amygdalin used, gram.	HCN formed,* gram.	Amygdalin decomposed, per cent.	$0{\cdot}4343K = 1/t \log a/a-x$.
10	0·05	0·00138	0·0252	0·0304
10	0·03	0·00085	0·0155	0·0315
10	0·02	0·00053	0·0097	0·0297

* Estimated by means of $N/100$ iodine.

Table XI.

Inhibition of the Hydrolysis by Means of Dextrose.

For each experiment, 20 c.c. of amygdalin solution (2 per cent.) were mixed with 1 c.c. of emulsin (2 per cent.).

Temp. = 40·0°.

Time of action, mins.	Dextrose added, gram.	Dextrose in gram-mol.	HCN formed, gram.	Amygdalin decomposed, per cent.
30	—	—	0·00319	13·5
30	0·2	0·0011	0·00314	13·3
30	0·4	0·0022	0·00298	12·6
30	0·75	0·0042	0·00279	11·8
30	1·0	0·0055	0·00274	11·6

Table XII.

Inhibition of the Hydrolysis by Means of Benzaldehyde.

For these experiments, a saturated solution of benzaldehyde was added to 20 c.c. of amygdalin (2 per cent.), mixed with 2 c.c. of emulsin solution (2 per cent.).

Vol. = 50 c.c. Temp. = 40·5°

Time of action, mins.	Benzaldehyde added,* c.c.	Benzaldehyde in gram-mols.	HCN formed, gram.	Amygdalin decomposed, per cent.
30	—	—	0·00613	26·0
30	1	$10^{-4} \times 0{\cdot}314$	0·00599	25·8
30	5	$10^{-4} \times 1{\cdot}570$	0·00545	23·1
30	10	$10^{-4} \times 3{\cdot}141$	0·00511	21·7
30	15	$10^{-4} \times 4{\cdot}715$	0·00471	20·0

* Benzaldehyde dissolved in 300 vols. of water.

TABLES XIII AND XIV.

Inhibition of the Hydrolysis by Means of Hydrocyanic Acid.

The hydrocyanic acid solution employed was found, on exact determination, to contain 0·112 per cent. of HCN. It was added to 20 c.c. of amygdalin solution (2 per cent.) mixed with 2 c.c. of the enzyme solution (2 per cent.).

Vol. = 50 c.c. Temp. = 40·0°.

Time of action, mins.	HCN added, c.c.	HCN in gram-mol.	HCN formed, gram.	Amygdalin decomposed, per cent.
30	—	—	0·00587	24·9
30	1	$10^{-4} \times 0{\cdot}42$	0·00612	25·9
30	3	$10^{-4} \times 1{\cdot}24$	0·00592	25·1
30	5	$10^{-4} \times 2{\cdot}07$	0·00574	24·3
30	10	$10^{-4} \times 4{\cdot}20$	0·00552	23·4

It will be observed that small quantities of hydrocyanic acid have a distinct accelerating effect on the action, and the following series of experiments may be quoted in which this action is intensified:

Temp. = 39·5°.

Time of action, mins.	HCN added, c.c.	HCN formed, gram.	Amygdalin decomposed, per cent.
30	—	0·01358	57·5
30	1·0	0·01391	59·0
30	3·0	0·01298	56·7
30	5·0	0·01338	55·0

TABLE XV.

Inhibition of the Hydrolysis by Means of the Mixed Products of Reaction.

Forty c.c. of 2 per cent amygdalin solution were mixed with 5 c.c. of emulsin solution, and the mixture kept in the thermostat at 40° in a stoppered bottle for four hours. The vessel and its contents were then heated for half an hour at 100° to destroy the enzyme, and then cooled to the ordinary temperature: 86 per cent. of the amygdalin had been decomposed. The product thus obtained was used for the inhibition experiments. For each estimation, 20 c.c. of amygdalin solution (2 per cent.) were mixed with 2 c.c. of emulsin (2 per cent.).

Temp. = 40·0°.

Time of action, mins.	"Reaction products" added, c.c.	Reaction products in gram-mol.*	HCN formed, gram.	Amygdalin decomposed, per cent.
30	—	—	0·00645	27·2
30	2	$10^{-4} \times 0{\cdot}770$	0·00605	25·6
30	5	$10^{-4} \times 1{\cdot}675$	0·00562	23·8
30	10	$10^{-4} \times 3{\cdot}850$	0·00491	20·8

* Calculated as amygdalin.

Inhibition of the Hydrolysis by Acids and Alkalis.

TABLE XVI.

N/50 Sulphuric Acid.

For each experiment, 15 c.c. of amygdalin solution (2 per cent.) were mixed with 3 c.c. of emulsin solution (1 per cent.).

Temp. = 40·0°. Vol. = 50 c.c.

No. of experiment.	Time of action, mins.	H_2SO_4 added, c.c.	HCN formed, gram.	Amygdalin decomposed, per cent.
1	15	—	0·00255	15·5
2	15	1	0·00241	14·6
3	15	2	0·00248	15·1
4	15	3	0·00223	13·6
5	15	5	0·00047	2·8
6	15	10	0·00011	0·6
7	15	15	—	—
8	15	20	—	—

Nos. 7 and 8 were exactly neutralised with dilute sodium hydroxide, and the mixture allowed to remain for another fifteen minutes at the same temperature. At the end of that time, No. 7 showed a decomposition of 3·4 per cent. of the amygdalin. After standing for a longer period, the odour of bitter almonds became very strong, showing the presence of a considerable quantity of active emulsin. No. 8 required a longer time for the signs of decomposition to appear.

TABLE XVII.

N/20 Hydrochloric Acid.

Quantities as before.

Temp. = 40·0°.

No. of experiment.	Time of action, mins.	HCl added, c.c.	HCN formed, gram.	Amygdalin decomposed, per cent.
1	15	—	0·00257	15·6
2	15	1	0·00192	11·6
3	15	2	0·00045	2·7
4	15	3	0 00015	0 9
5	20	5	—	—
6	10	10	—	—

As in the previous case, the last two experiments of the series were completed by exactly neutralising the liquid with sodium hydroxide and allowing the action to proceed as before. It was again found that the emulsin had been re-activated, although only to a small extent. No. 5 showed a decomposition of about 4 per cent. after fifteen minutes at 40°, but the activity of the emulsin in No. 6 had been nearly destroyed, for only after many hours was a faint odour of bitter almonds detectable.

TABLE XVIII.

N/20 Acetic Acid.

Quantities as before.

Temp. = 40·5°. (New 1 per cent. emulsin solution used.)

Time of action, mins.	Acetic acid added, c.c.	HCN formed, gram.	Amygdalin decomposed, per cent.
15	—	0·00291	17·7
15	1	0·00261	15·9
15	2	0·00250	15·2
15	3	0·00232	14·1
15	5	0·00207	12·6
15	10	0·00178	10·8
15	15	0·00135	8·2

TABLE XIX.

N/20 Lactic Acid.

Quantities as before.

Temp. 40·5°.

Time of action, mins.	Lactic acid added, c.c.	HCN formed, gram.	Amygdalin decomposed, per cent.
15	—	0·00293	17·8
15	1	0·00268	16·3
15	3	0·00214	13·3
15	5	0·00192	12·7
15	10	0·00144	8·7
15	15	0·00097	5·9
15	20	0·00056	4·0

Bouchardat (*Comp rend.*, 1845, **20**, 111) has stated that acetic acid has no effect on the hydrolysis of amygdalin by emulsin, but from the above tables it is obvious that this empirical statement is erroneous, and that both acetic and lactic acids have a distinct inhibiting effect.

TABLE XX.

N/50 Potassium Hydroxide.

For each experiment, 15 c.c. of amygdalin solution (2 per cent.) were mixed with 3 c.c. of emulsin (1 per cent.).

Vol. = 50 c.c. Temp. = 40·5°.

No. of experiment.	Time of action, mins.	KHO added, c.c.	HCN formed, gram.	Amygdalin decomposed per cent.
1	15	—	0·00293	17·8
2	15	1	0·00275	16·7
3	15	2	0·00194	11·7
4	15	3	0·00025	1·5
5	15	5	—	—
6	15	10	—	—

After fifteen minutes, No. 6 was exactly neutralised with dilute hydrochloric acid, and allowed to remain in the thermostat for a further twenty-five minutes. At the end of that time a very strong odour of benzaldehyde and hydrocyanic acid could be detected, and on examination it was found that nearly 8 per cent. of the amygdalin had been decomposed. To confirm this remarkable re-activating of the emulsin, further experiments on neutralisation of the alkali were carried out.

TABLE XXI.

Quantities as before.

Temp. = 40·5°.

No. of expt.	KHO added, c.c.	Time of action of KHO, mins.	Time of action after neutralisation, mins.	HCN formed after neutralisation, gram.	Amygdalin decomposed after neutralisation, per cent.
6*	10	15	25	0·00131	7·9
7	10	30	30	0·00094	5·6
8	15	15	30	0·00125	7·6
9	20	20	30	0·00104	6·2

* Table XX.

Similar results to the above were obtained with a saturated solution of sodium hydrogen carbonate, the re-activation being very marked. The experiments were carried out originally when studying the inhibiting action of sodium hydrogen carbonate with a view to its utility for stopping the emulsin action. In experiments Nos. 3, 4, and 5, in table I, half the experimental liquid was used for determination of the hydrocyanic acid, and the remainder neutralised with hydrochloric acid, and replaced in the thermostat.

TABLE XXII.

N-*Sodium Hydrogen Carbonate.*

No. of expt.	Time of action, mins.	HCN formed, gram.	Amygdalin decomposed, per cent.
3	20	0·0046	24·4
4	20	0·0041	21·7
5	20	0·0039	20·1

Extent of the Hydrolysis.

TABLE XXIII.

Temp. = 40·0°.

Time of action, hours.	Emulsin added (2 per cent.), c.c.	Amygdalin solution (2 per cent.), c.c.	Decomposition from HCN, per cent.	Decomposition from $C_6H_5 \cdot CHO$, per cent.
20	10	75	93·4	94·0
24	15	75	97·0	96·5
16	3	15	91·7	91·0

Temperature Coefficients.

TABLE XXIV.

In the first columns are given the times of the reaction (t), in the second the amount of hydrocyanic acid formed, in grams, and in the third the amount of amygdalin decomposed, per cent.

$T = 15^\circ$.

t.	HCN.	D.
15	0·00077	4·68
30	0·00160	9·40
45	0·00230	14·00

$T = 20^\circ$.

t.	HCN.	D.
15	0·00149	9·06
30	0·00286	17·40
45	0·00429	26·10

$T = 25^\circ$.

t.	HCN.	D.
15	0·00177	10·77
30	0·00355	21·60

$T = 30^\circ$.

t.	HCN.	D.
15	0·00250	15·21
30	0·00492	30·00

$T = 35^\circ$.

t.	HCN.	D.
15	0·00356	21·66
30	0·00679	41·30

$T = 40^\circ$.

t.	HCN.	D.
15	0·00400	24·33
30	0·00785	47·77

$T = 45^\circ$.

t.	HCN.	D.
15	0·00470	28·46
20	0·00890	53·07

$T = 50^\circ$.

t.	HCN.	D.
10	0·00413	25·51
15	0·00625	38·04
30	0·01081	65·82

$T = 55^\circ$.

t.	HCN.	D.
15	0·00486	29·58

$T = 60^\circ$.

t.	HCN.	D.
10	0·00300	18·30
15	0·00445	27·08

The values of K, calculated for each temperature from the fifteen minute decomposition values are given in the following table, together with the ten-degree ratios calculated from them.

TABLE XXV.

Temperature.	K.	k_{t+10}/k_t.	Tammaun's value for salicin.
15°	0·01393	$k_{25}/k_{15} = 2·37$	
20	0·02635	$k_{30}/k_{20} = 1·81$	2·52
25	0·03299	$k_{35}/k_{25} = 2·14$	
30	0·04777	$k_{40}/k_{30} = 1·68$	1·52
35	0·07068	$k_{45}/k_{35} = 1·37$	
40	0·08071	$k_{50}/k_{40} = 1·71$	1·79
45	0·09696	$k_{55}/k_{45} = 1·04$	
50	0·13840		
55	0·10152		
60	0·09142		
72—73	nil *		

* Henry and Auld (*loc. cit.*).

CHEMICAL DEPARTMENT,
EAST LONDON COLLEGE.

CXXI.—*The Hydrolysis of Amygdalin by Emulsin. Part II.*

By S. J. Manson Auld, Ph.D.

By the action of an extract of yeast (Hefenenzym), amygdalin is hydrolysed with the separation of only one molecule of glucose and the formation of a true glucoside, mandelonitrile glucoside (Fischer, *Ber.*, 1899, **28**, 1509):

$$C_{20}H_{27}O_{11}N + H_2O = C_6H_{12}O_6 + C_{14}H_{17}O_6N.$$

Mandelonitrile glucoside is hydrolysed by emulsin into benzaldehyde, hydrocyanic acid, and glucose.

From the above decomposition of amygdalin by yeast extract, the active enzyme of which was supposed to be maltase * (the ferment which decomposes maltose into two molecules of glucose), Fischer assumed that amygdalin is a derivative of maltose or of an exactly similarly constructed sugar. Latterly it has been generally the custom to regard amygdalin as the maltoside of benzaldehydecyanohydrin, and as such it is described in most books of reference. Thanks chiefly to the work of Emil Fischer, it is now practically certain that whilst emulsin only decomposes β-glucosides, maltase will only hydrolyse those glucosides which are derived from α-dextrose, hence there exists a distinct stereochemical relationship between these sugars and their specific enzymic hydrolysts.

These facts seemed to render it probable, or indeed certain, that the two molecules of glucose in the biose residue of amygdalin are not of similar constitution owing to their different behaviour towards the complementary enzymes, emulsin and maltase. It was first pointed out by the author (Proc., 1907, **23**, 72) that amygdalin is probably the derivative of an unknown αβ-disaccharide capable of hydrolysis both by emulsin (β-enzyme) and maltase or amygdalase (α-enzyme). This view has since been confirmed by Rosenthaler (*Arch. Pharm.*, 1907, **245**, 684). It was also pointed out that in the hydrolysis of amygdalin by emulsin the decomposition could take place in three ways, depending on the mode of attachment of the enzyme to the glucoside molecule. Either mandelonitrile glucoside and dextrose are first produced with subsequent hydrolysis of the former, or benzaldehydecyanohydrin and the disaccharide are formed and the latter then resolves into two molecules of dextrose, or, lastly, amygdalin may undergo fission into the three components by direct abstraction of the dextrose residue attached to the benzaldehydecyanohydrin molecule.

---

* It has now been shown by Caldwell and Courtauld (*Proc. Roy. Soc.*, 1907, **79**, *B*, 350) that the yeast enzyme which hydrolyses amygdalin is not identical with maltase. This, however, has no effect on the above arguments as "amygdalase" is also an α-enzyme.

Thanks to the admirable work of E. F. Armstrong on the correlation of the stereoisomeric α- and β-glucosides with the corresponding glucoses (Trans., 1903, **83**, 1305), the first part of the problem could be attacked in the same manner as was adopted for the determination of the structure of the α-glucoside phaseolunatin (Dunstan, Henry, and Auld, *Proc. Roy. Soc.*, 1907, **79**, *B*, 315). This method depends on the formation of sugar from the glucoside by hydrolysis and observation of its change of rotation on assuming the ordinary form of glucose which has been shown by Lowry (Trans., 1903, **83**, 1314) to be an equilibrium mixture of two stereoisomerides. The production of equilibrium is hastened by the addition of a drop of alkali.

Rotation of Amygdalin.—With regard to the optical rotation of amygdalin, two different numbers are recorded. Bouchardat (*Compt. rend.*, 1844, **19**, 1175) found for amygdalin, dried over lime at 45°, $[\alpha]_D$ −35·5°, and this value is still quoted in many books of reference. Schiff (*Ber.*, 1899, **32**, 2701), repeating the experiments, obtained the value −40·26°, and declared Bouchardat's figures to refer to $[\alpha]_B$ and not to $[\alpha]_D$. Owing to these different results, the rotation of amygdalin was carefully measured, with the result that Schiff's rotations were also found to be not quite correct, the average rotation found being $[\alpha]_D$ − 41°36′. For 3·883 per cent. Schiff found $[\alpha]_D$ − 41·1°.

Amygdalin, per cent.	*l.*	α_D^{18}.	$[\alpha]_D^{18}$.	(Schiff.) $[\alpha]_D^{17}$.	$[\alpha]_D$ calculated from Bouchardat's results by Schiff.
1·636	200	1°22′	41°16′	—	—
3·272	200	2 45	42 1	40°18′	41°57′
5·418	200	4 30	41 31	—	—

Mean = 41°36′.

Characterisation of the Dextrose Residues in Amygdalin.—Owing to the comparative slowness with which the yeast enzyme attacks amygdalin and the consequent spontaneous production of equilibrium in the dextrose which is formed together with the one molecule of mandelonitrile glucoside, it was found impossible to identify the sugar by the method proposed by E. F. Armstrong. To determine the nature of the second dextrose molecule, namely, that attached to the benzaldehydecyanohydrin nucleus, the decomposition of mandelonitrile glucoside by emulsin was employed. The mandelonitrile glucoside was prepared from amygdalin by the action of yeast extract according to the directions given by Fischer (*Ber.*, 1895, **28**, 1509). After recrystallisation from chloroform it melted at 148°, and a proof of its purity was obtained by analysis. 0·5 Gram of emulsin was added to 5 grams of mandelonitrile glucoside dissolved in 50 c.c. of water, thoroughly mixed by shaking and kept in the thermostat in a stoppered bottle at 40°. For each observation, a few c.c. of the liquid were withdrawn, mixed with a small definite volume of alumina cream, and filtered through asbestos. The rotation of the clear liquid was then observed, before and after adding a drop of ammonia solution to establish equilibrium. Great care was taken to avoid the presence of any traces of alkali which might induce premature equilibrium, as in some cases it was found that the presence of a small proportion of tap-water was sufficient immediately to cause the dynamic change:

Time of action, hours.	Initial rotation.	Rotation after adding alkali.	Change of rotation.
—	−1°48′	−1°48′	0°0′
0·5	−1 18	−1 4	+0 14
1·0	−0 45	−0 20	+0 25
1·5	−0 22	+0 2	+0 24
24·0	+0 32	+0 35	+0 3

Taking into account the following rotations:

Mandelonitrile glucoside	−26·1°
α-Glucose	+105·0
β-Glucose	+22·0
Equilibrium mixture of α- + β-glucose	+52·5

it is obvious from the results set forth above that in the decomposition of mandelonitrile glucoside there is primarily liberated the low rotating β-glucose, which, on the addition of ammonia, is at once transformed into the equilibrium mixture of higher rotation, thus proving, what has been generally assumed, that Fischer's glucoside is a β-glucoside. As a result of this, it is certain also that the dextrose residue of the amygdalin biose which is attached to the benzaldehydecyanohydrin nucleus has also a β-configuration.

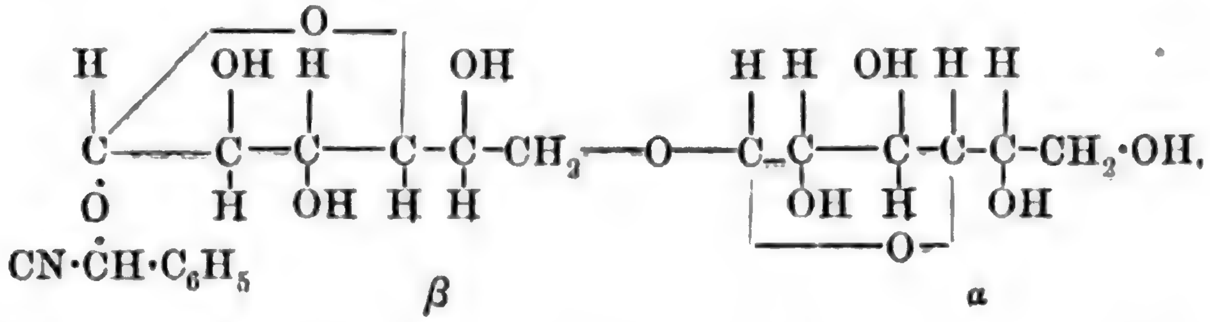
Although, as mentioned previously, it is impossible similarly to obtain direct evidence of the remaining dextrose molecule, the result can be attained by utilising the decomposition of amygdalin itself in a manner similar to that used for mandelonitrile glucoside. If both molecules of the biose are of β-configuration the positive change in rotation should be greatly increased, whereas, if the second molecule is derived from α-glucose, the optical rotation of the sugars produced on liberation with emulsin will to a certain extent neutralise each other, and on production of the equilibrium there will be no change, or only a very slight decrease in the rotation. This was actually found to be the case, as by using strong solutions of amygdalin a slight decrease in the rotation could be detected:

Temperature = 40·5°.

Weight of amygdalin in 50 c.c. of H_2O, grams.	Weight of emulsin added, gram.	Time of action, hours.	Initial rotation,	Rotation after adding alkali.	Change of rotation.
4·45	0·3	—	– 6°48′	– 6°48′	0° 0′
4·45	0·3	0·5	– 3 54	– 4 4	– 0 10
4·45	0·3	1·0	– 1 30	– 1 45	– 0 15
4·45	0·3	2·0	+ 2 51	+ 2 43	– 0 8
4·45	0·3	24·0	+ 6 26	+ 6 26	– 0 0
3·8	0·25	—	– 4 48	– 4 48	– 0 0
3·8	0·25	0·66	– 3 9	– 3 18	– 0 9
3·8	0·25	1·33	– 0 23	– 0 33	– 0 10
3·8	0·25	20·0	+ 2 14	+ 2 14	0 0

Rotations measured in 2-dcm. tube.

From these results it would therefore seem to have been definitely proved that the biose from which amygdalin is derived is not maltose, but an *αβ*-diglucose, and that amygdalin should be formulated as follows:



Of extreme interest in this connexion is the fact, made apparent by the following experiments, that maltose, unlike glucose, has practically no inhibiting effect on the hydrolysis of amygdalin by emulsin.

Effect of Maltose on the Velocity of Hydrolysis.—For each experiment, 15 c.c. of 2 per cent. amygdalin solution were mixed with 3 c.c. of emulsin solution:

Temperature = 41·5°.

Time of action, mins.	Maltose added, gram.	HCN formed, gram.	Amygdalin decomposed, per cent.
30	—	0·00287	17·46
30	0·05	0·00284	17·27
30	0·10	0·00281	17·10
30	0·20	0·00283	17·23
30	0·30	0·00280	17·04

Mode of Procedure of the Hydrolysis.—Taking into account the three possible methods of decomposing amygdalin by emulsin, it will be observed that each involves the production of different quantities of the end-products. If mandelonitrile glucoside is formed as an intermediate product of the reaction and is hydrolysed more slowly than amygdalin (which seems to be the case), then estimation of the hydrocyanic acid and the benzaldehyde formed should give (relatively) lower results than those obtained from the dextrose. The same holds good in the equilibrium stage of the hydrolysis, as practically no enzyme action is complete and consequently a certain amount of the intermediate product may be expected to remain undecomposed. Similarly, should the emulsin after attaching itself to the *β*-glucoside molecule, as it apparently must do in its rôle of *β*-enzyme, cause the intermediate formation of the unknown *αβ*-disaccharide, then the dextrose estimations should fall below those of the hydrocyanic acid and benzaldehyde; only in the event of the enzyme causing the disruption of the amygdalin molecule by simultaneous cleavage of the "biose" and "cyanohydrin" linkings would hydrocyanic acid, benzaldehyde, and dextrose be formed in quantities corresponding with the ordinary equation of amygdalin hydrolysis. It will be observed that the first method leads to the apparent anomaly of amygdalin being decomposed in the same manner by both yeast enzyme (Caldwell and Courtauld's amygdalase) and emulsin, which enzymes are of course really complementary to each other in their action. From one or two preliminary experiments carried out it was originally thought that the biose was formed as an intermediate product. This view, however, had to be considerably modified after careful and exhaustive series of experiments had been carried out. It was eventually found, in fact, that estimations of hydrocyanic acid and benzaldehyde constantly gave lower results than those of dextrose.

Care had to be taken to obtain the maximum hydrolysis in as short a time as possible so as to avoid any error due to partial decomposition of hydrocyanic acid on standing. A correction had also to be applied for the reducing power of the enzyme added, which was found to be considerable.

To avoid repetition and to save space, only a certain number of the results obtained will be quoted, and all these are included in the following table:

Time of action, hours.	Amygdalin used, grams.	Emulsin used, gram.	HCN formed, gram.	Cu_2O formed (corrected), grams.	Decomposition from HCN, per cent.	Decomposition from $C_6H_{12}O_6$, per cent.*	Decomposition from $C_6H_5{\cdot}CHO$, per cent.†
0·5	0·4	0·03	0·00556	0·6090	23·5	27·8	—
1·0	0·4	0·03	0·01000	1·0520	42·5	48·0	—
1·25	0·4	0·03	0·01187	1·2800	50·2	58·4	49·9
2·25	0·4	0·03	0·01772	1·8610	75·0	85·1	75·8
16·0	1·2	0·10	0·06501	—	91·7	—	91·0
20·0	1·5	0·20	0·07665	2·0800	93·4	94·9	94·0
4·0	0·3	0·06	0·01430	1·9900	87·0	90·8	—
1·75	0·3	0·06	0·01330	1·9300	81·5	88·1	—
0·25	0·3	0·04	0·00469	—	28·4	—	28·6
24·0	1·5	0·30	0·07969	2·1358	97·0	97·5	96·5

* Estimated gravimetrically. † Estimated by Ripper's method.

These results make it appear certain that the reaction proceeds (at any rate mostly) in two stages, and that the biose linking in amygdalin is less resistant towards emulsin than that of the benzaldehydecyanohydrin. In this way mandelonitrile glucoside is formed preferentially and should appear among the reaction products. By stopping the reaction at a suitable stage, Fischer's glucoside can actually be separated. 0·5 Gram of emulsin was allowed to act on 20 grams of amygdalin and the reaction stopped when 75 per cent. of the amygdalin had been decomposed as calculated from the hydrocyanic acid liberated. The liquid was boiled to coagulate the protein matter, filtered and evaporated to dryness with animal charcoal, the charcoal being subsequently extracted with dry ethyl acetate. After repeating this process, the concentrated syrup was allowed to stand, when the mandelonitrile glucoside separated in small needles, melting, after recrystallisation, at 148°.

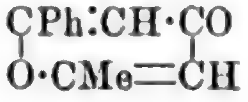
Considering this remarkable intermediate formation of mandelonitrile glucoside in the hydrolysis of amygdalin by emulsin, which is thus identical with that of acids (Caldwell and Courtauld, Trans., 1907, **91**, 666), it is curious that Fischer's glucoside has not so far been discovered co-existent with amygdalin in Nature.

CHEMICAL DEPARTMENT,
EAST LONDON COLLEGE.

CXXII.—*The Formation of 4-Pyrone Compounds from Acetylenic Acids. Part II.*

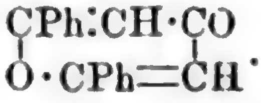
By SIEGFRIED RUHEMANN.

RECENTLY (Trans., 1908, **93**, 431) I have described a method of formation of 4-pyrone compounds, which is based on the reaction between ketones and ethyl phenylpropiolate in the presence of sodium ethoxide. Thus, two members of this group of substances have been obtained, namely, 2-phenyl-6-methyl-4-pyrone (I) and 2 : 6-diphenyl-4-pyrone (II) :



$$\begin{array}{l}\mathrm{CPh{:}CH{\cdot}CO} \\ \mathrm{O{\cdot}CMe{=}CH}\end{array}$$

(I.)



$$\begin{array}{l}\mathrm{CPh{:}CH{\cdot}CO} \\ \mathrm{O{\cdot}CPh{=}CH}\end{array}$$

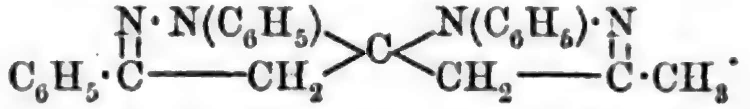
(II.)

I have mentioned also (*loc. cit.*) that the formation of diphenylpyrone is accompanied by the production of a compound, $C_{25}H_{25}O_8$, which is characterised by the violet coloration of its solution in concentrated sulphuric acid. I have frequently studied the action of sodium ethoxide on the mixture of acetone and ethyl phenylpropiolate without having been able to trace a compound with similar properties; the product of the reaction consists of phenylmethylpyrone, the yield of which amounts to 48—50 per cent., of the unchanged acetylenic ester, and the corresponding acid.

The present paper deals with the study of phenylmethylpyrone, which I have carried out on lines similar to those adopted by F. Feist (*Annalen*, 1890, **257**, 253) in his work on 2 : 6-dimethyl-4-pyrone. He showed that this compound, on treatment with baryta, is transformed into the yellow barium salt of diacetylacetone, which, with hydrochloric acid, yields the colourless triketone, $(CH_3{\cdot}CO{\cdot}CH_2)_2CO$. He has not been able to accomplish the analogous change on using diphenylpyrone owing to the insolubility of this pyrone in water (compare *Ber.*, 1890, **23**, 3726). I have repeated this experiment, but have also failed to isolate the triketone, dibenzoylacetone, from the product of the action of baryta on the pyrone. Phenylmethylpyrone, however, is readily transformed into a yellow barium salt, which, with hydrochloric acid, yields *benzoylacetylacetone*,

$$C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_3.$$

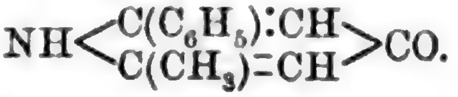
This compound resembles diacetylacetone in its behaviour. Feist has found (*loc. cit.*) that the latter triketone forms, with phenylhydrazine, a yellow diphenylhydrazone, which is produced, also, by the action of the hydrazine on 2 : 6-dimethyl-4-pyronecarboxylic acid; in this case, however, a colourless substance is formed at the same time which contains one molecule of water less than the dihydrazone. A compound, which in composition and properties resembles this substance, is produced on treatment of benzoylacetylacetone with phenylhydrazine. The fact that this compound is very stable and only slightly reduces Fehling's solution, even on boiling, points to the constitution:



$$\begin{array}{r}N{\cdot}N(C_6H_5)\\ \| \quad\quad\quad\\ C_6H_5{\cdot}C{-\!-\!-}CH_2\end{array}\!\!>C<\!\!\begin{array}{l}N(C_6H_5){\cdot}N\\ \quad\quad\quad\;\|\\ CH_2{-\!-\!-}C{\cdot}CH_3\end{array}.$$

This corresponds with the formula suggested by Feist for the colourless compound which is formed from dimethylpyronecarboxylic acid.

By the action of ammonia, benzoylacetylacetone is transformed into 2-*phenyl*-6-*methyl*-4-*pyridone*,



$$NH<\begin{matrix}C(C_6H_5){:}CH\\C(CH_3){=}CH\end{matrix}>CO.$$

This substance has a characteristic behaviour which neither pyridone nor its dimethyl derivative seems to possess, namely, that its aqueous solutions readily gelatinise; this property renders its purification somewhat troublesome. I have prepared several salts of this base, but none of them exhibits this phenomenon. The ease with which β-diketones, for example, acetylacetone, react with aldehydes has induced me to ascertain whether benzoylacetylacetone shows a similar behaviour; I have found, however, that in the presence of neither piperidine nor sodium hydroxide as catalytic agent does this triketone condense with benzaldehyde or salicylaldehyde.

EXPERIMENTAL.

Benzoylacetylacetone, $C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_3$.

On adding a concentrated aqueous solution of baryta to phenylmethylpyrone dissolved in boiling water, a yellow barium salt is precipitated which, when added to dilute hydrochloric acid, loses its colour and is transformed into benzoylacetylacetone. This substance is sparingly soluble in carbon disulphide, ether, or cold alcohol, but readily dissolves in boiling alcohol or chloroform; it crystallises from light petroleum, in which on boiling it is fairly soluble, in pale brown needles melting at 106—107°:

0·2213 gave 0·5716 CO_2 and 0·1182 H_2O. C = 70·44; H = 5·93.

$C_{12}H_{12}O_3$ requires C = 70·59; H = 5·88 per cent.

The triketone is readily dissolved by dilute potassium hydroxide, yielding a yellow solution; it is insoluble in cold, but soluble in hot sodium carbonate solution.

Action of Phenylhydrazine on Benzoylacetylacetone.

On adding water to the mixture of the triketone (1 gram), dissolved in alcohol, and phenylhydrazine (1·2 grams), an oily product is precipitated which, when stirred with alcohol, sets to a yellow solid. This is sparingly soluble in boiling alcohol, and, on cooling, crystallises in colourless prisms melting at 174—175°:

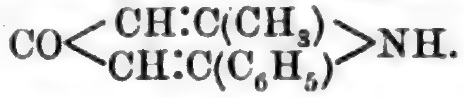
0·2015 gave 0·5800 CO_2 and 0·1100 H_2O. C = 78·50; H = 6·06.

0·2265 ,, 30 c.c. N_2 (moist) at 17° and 756 mm. N = 15·28.

$C_{24}H_{22}N_4$ requires C = 78·69; H = 6·01; N = 15·30 per cent.

The formation of this substance is most probably proceeded by the production of the diphenylhydrazone of benzoylacetylacetone, which, however, at once condenses with loss of water. The fact that this compound is but slightly attacked by potassium hydroxide or hydrochloric acid, and only faintly reduces Fehling's solution on boiling, seems to support the formula given on p. 1282.

2-*Phenyl*-6-*methyl*-4-*pyridone*,



$$CO<\begin{matrix}CH:C(CH_3)\\CH:C(C_6H_5)\end{matrix}>NH.$$

Benzoylacetylacetone is readily soluble in hot, concentrated ammonia; on evaporating the solution on the water-bath, a solid is left behind which is sparingly soluble in cold, but readily so in boiling water. The hot concentrated solution, after treatment with animal charcoal, deposits colourless, curved needles, and the mother liquor, after a short time, sets to a jelly which renders it impossible to collect the crystals. It is therefore necessary to filter them from the warm solution. The pyridone melts at 177—178°:

0·2100 gave 0·5970 CO_2 and 0·1155 H_2O. C = 77·53; H = 6·11.
0·2230 „ 14·8 c.c. N_2 (moist) at 18° and 755 mm. N = 7·61.
$C_{12}H_{11}ON$ requires C = 77·84. H = 5·95; N = 7·57 per cent.

The gelatinous product which separates from the mother liquor of the crystals seems to contain the same substance; this would follow from the fact that the solid which is left behind, on evaporation to dryness, gave the following analytical data:

0·2172 gave 0·6138 CO_2 and 0·1182 H_2O. C = 77·07; H = 6·04,

which do not appreciably differ from those required for phenylmethylpyridone.

The pyridone dissolves in hot, concentrated hydrochloric acid, and the solution, on cooling, deposits colourless needles of the *hydrochloride*. This melts at 242°, after having begun to soften at 225°; it is not very soluble in cold, but readily so in boiling water:

0·2340 gave 0·1518 AgCl. Cl = 16·05.
$C_{12}H_{11}ON,HCl$ requires Cl = 16·03 per cent.

On adding platinum tetrachloride to the aqueous solution of the hydrochloride, the *platinichloride* of the pyridone is precipitated in pale orange, microscopic needles:

0·3048 gave 9·6 c.c. N_2 (moist) at 19° and 764 mm. N = 3·65.
0·2068 left on ignition 0·0520 Pt. Pt = 25·09.
$(C_{12}H_{11}ON)_2,H_2PtCl_6$ requires N = 3·59. Pt = 24·94 per cent.

The *picrate* is formed on mixing aqueous solutions of phenylmethylpyridone and picric acid. The emulsion which is first produced, soon sets to a crystalline solid, which is sparingly soluble in cold, but fairly readily in boiling water, and, on cooling, separates in yellow needles melting at 194—195°:

0·1986 gave 24 c.c. N_2 (moist) at 20° and 753 mm. N = 13·59.
$C_{12}H_{11}ON,C_6H_3O_7N_3$ requires N = 13·52 per cent.

The *chromate* is precipitated in orange needles on adding chromic acid, dissolved in water, to the aqueous solution of the pyridone:

0·2368 gave 10 c.c. N_2 (moist) at 19° and 754 mm. N = 4·81.

$(C_{12}H_{11}ON)_2,H_2Cr_2O_7$ requires N = 4·75 per cent.

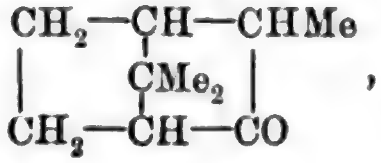
The salt does not melt, but, on heating, begins to blacken at about 155°; it is sparingly soluble in cold, but readily so in boiling water.

GONVILLE AND CAIUS COLLEGE,
CAMBRIDGE.

CXXIII.—*α-Methylcamphor and Fenchone.*

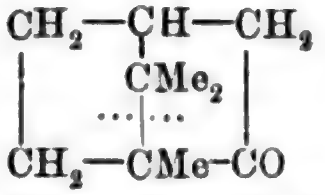
By WALTER HAMIS GLOVER.

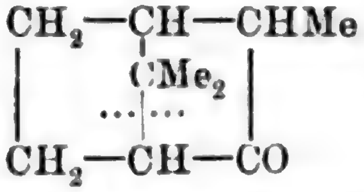
THE investigation described in this communication was undertaken primarily with the object of contrasting α-methylcamphor with fenchone, to which Wallach has assigned the formula



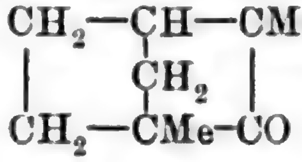
mainly because *m*-cymene is formed when it is heated with phosphoric oxide (*Annalen*, 1898, **300**, 319). If fenchone possess the constitution represented by this formula, it should be similar to α-methylcamphor in its general chemical behaviour, as it is not to be supposed that the transference of a methyl radicle to the α-position would tend to alter the properties of the compound materially. As a matter of fact, the two substances are essentially different in chemical behaviour. They differ most markedly in their behaviour towards bromine. Minguin has stated (*Compt. rend.*, 1903, **136**, 751)—and his observations have been confirmed—that α-methylcamphor yields on bromination a well-defined monobromo-derivative, namely, α′-bromo-α-methylcamphor; fenchone, when similarly treated, does not yield a bromo-derivative: in fact, bromofenchone is obtained as a somewhat ill-defined oil only when fenchone is heated with bromine in sealed tubes at 100° for twenty hours (Czerny, *Ber.*, 1900, **33**, 2287). The two compounds also differ in that α-methylcamphor is as readily sulphonated by Reychler's method (*Bull. Soc. chim.*, 1898, [iii], **19**, 120) as camphor itself, whilst fenchone resists sulphonation.

These two facts are alone sufficient to make it more than doubtful whether the constitution of fenchone be that suggested by Wallach, The objection may also be raised to Wallach's formula that, since camphor yields *p*-cymene, fenchone should yield ortho-, not meta-, cymene:



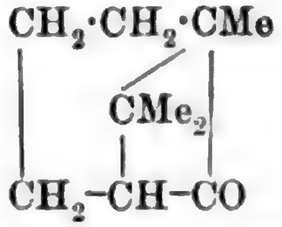


Semmler (*Chem. Zeit.*, 1905, **29**, 1313), arguing from the fact that *iso*camphoronic acid, dimethylcarballylic acid and dimethylmalonic acid are products of oxidation of fenchone, has concluded that Wallach's formula is incorrect and has put forward the following:



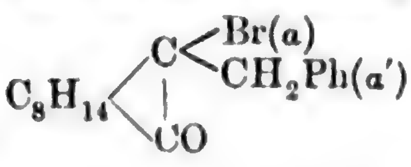
Although this formula foreshadows the difficulty with which fenchone is brominated, there is no obvious reason why such a compound should not yield a *β*-sulphonic acid with the same readiness as *a*-methylcamphor; moreover, the formula in no way gives expression to the production of *m*-cymene.

It is suggested that the following formula would better represent the formation of this hydrocarbon and would likewise show why fenchone should not be brominated readily nor be converted into a *β*-sulphonic acid by Reychler's method.

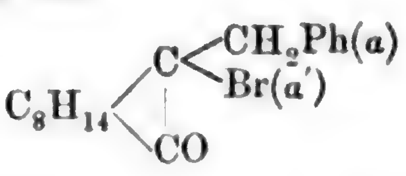


A monobromo-derivative of *a*-methylcamphor isomeric with that obtained directly from *a*-methylcamphor was prepared by Minguin (*loc. cit.*) by acting on methylenecamphor with a solution of hydrogen bromide in glacial acetic acid.

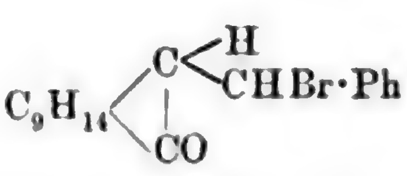
Haller and Minguin (*Compt. rend.*, 1900, **130**, 1362; 1901, **133**, 79) found that *a*-benzylcamphor on bromination gives rise to two stereoisomeric *a'*-bromo-*a*-benzylcamphors (I and II), which melt respectively at 94—95° and 90—91°; whilst the isomeride formed by adding hydrogen bromide to benzylidenecamphor is an *ω*-bromo-*a*-benzylcamphor (III) melting at 146°.



(I.)

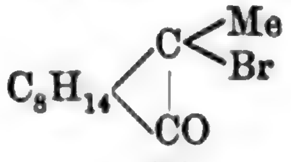


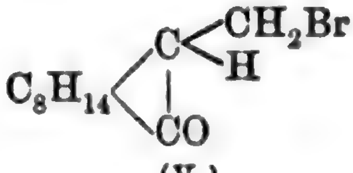
(II.)



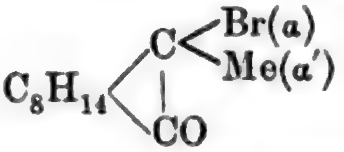
(III.)

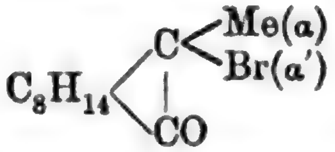
Minguin therefore supposed, on the assumption that *a*-methylcamphor was the analogue of *a*-benzylcamphor, that the compound obtained directly was α'-bromo-α-methylcamphor (IV) and that the isomeride was ω-bromo-α-methylcamphor (V).


(IV.)


(V.)

It seemed not improbable, however, that since these isomerides, like the isomeric α'-bromo-α-benzylcamphors, melt within a few degrees of each other, the melting points being 61° and 65° respectively, they might be stereoisomeric α'-bromo-α-methylcamphors, thus:





Now Lowry has shown (Trans., 1906, **89**, 1033) that α-mono-substituted derivatives of camphor, such as α-bromocamphor, are partly converted into their stereoisomeric forms by the addition of traces of sodium ethoxide to their alcoholic solutions, the change being accompanied by a change in the optical rotatory power of the solution. It therefore seemed possible that, by investigating the effect of alkali on the optical rotatory powers of alcoholic solutions of the two mono-bromo-derivatives of α-methylcamphor, the correctness, or otherwise, of the above supposition could be tested. However, neither of the alcoholic solutions of the isomerides showed any change in optical rotatory power on the addition of alkali, although, as was proved later, one of the isomerides is ω-bromo-α-methylcamphor as stated by Minguin (*loc. cit.*). Further examination of α-methylcamphor and its β-substituted derivatives showed that these compounds, although, still containing an atom of hydrogen in the α-position, apparently do not undergo stereoisomeric change in alcoholic solution under the influence of alkali. It appears not improbable therefore that, under these conditions, only those α-mono-substituted derivatives of camphor undergo stereoisomeric change in which the substituting radicle is strongly negative in character, as was the case in the compounds investigated by Lowry, unless it be that, in the above cases, the change takes place very rapidly before the addition of alkali and escapes observation.

The action of potassium permanganate on the isomerides was first investigated. Although both are but slightly affected by this agent, nevertheless, under similar conditions, it is noticeable that the colour of the permanganate is discharged more readily and that more bromide is found in solution in the case of the compound described by Minguin as ω-bromo-α-methylcamphor than in the case of α'-bromo-α-methylcamphor. Again, the former compound remains unaltered in the presence of cold nitric acid (sp. gr. 1·4), whereas the latter readily parts with its bromine when similarly treated. This difference in the behaviour of the two compounds being scarcely that to be expected in the case of stereoisomerides, their comparative study was continued: finally it was found possible to brominate one isomeride, namely, the ω-bromo-α-methylcamphor, whilst the other isomeride, α′-bromo-α-methylcamphor, remained unattacked.

The compound obtained by brominating ω-bromo-α-methylcamphor is ωα′-dibromo-α-methylcamphor, since it is identical with the compound obtained by the addition of bromine to methylenecamphor.

As regards the properties of the individual derivatives of α-methylcamphor described in this paper, little need be said. Generally speaking, they are very similar to the corresponding camphor compounds in their ordinary chemical and physical characteristics. As a rule, however, the melting point of the compound is lowered by the introduction of the methyl group into the α-position, whilst the specific rotatory power remains approximately the same; this will be seen by reference to the following table, in which are given the specific rotatory powers and melting points of the corresponding derivatives of *d*-camphor and α-methylcamphor.

Compound.	M. p.	$[\alpha]_D$.
Camphor	175°	+43° (alcohol)
α-Bromocamphor	76	+135 (alcohol)
Camphor-β-sulphonic acid	193	+21 (water)
Camphor-β-sulphonyl chloride	67—68	+31 (chloroform)
Camphor-β-sulphonamide	132	+1·5 (chloroform)
β-Bromocamphor	78	+19 (alcohol)
α-Methylcamphor	38	+30 (alcohol)
α′-Bromo-α-methylcamphor	62·5	+180 (alcohol)
α-Methylcamphor-β-sulphonic acid	114—116	+18 (water)
α-Methylcamphor-β-sulphonyl chloride	33	+29 (benzene)
α-Methylcamphor-β-sulphonamide	150	−6·3 (chloroform)
β-Bromo-α-methylcamphor	55	+18 (alcohol)

Thus, although the introduction of the methyl group into the α-position involves the production of a third asymmetric carbon atom within the molecule, no marked change in the rotatory power is induced. This is what might be expected, since the greater the dissimilarity of the radicles occupying the αα′-positions the greater is the change produced in the specific rotatory power of the compound. This is at once seen from the following examples:

Camphor	$[\alpha]_D$	+43°	α-Bromocamphor	$[\alpha]_D$	+135°
α-Methylcamphor	$[\alpha]_D$	+30	α-Chloro-α′-bromocamphor	$[\alpha]_D$	+10
α-Iodocamphor	$[\alpha]_D$	+160	αα′-Dibromocamphor	$[\alpha]_D$	+40

A great difference exists, however, between the specific rotatory powers of the oximes of the two compounds. As was shown by Beckmann (*Annalen*, 1889, **250**, 354), the oxime obtained from *d*-camphor has the specific rotatory power $[\alpha]_D$ −42°; that of the oxime prepared from α-methylcamphor is $[\alpha]_D$ +30° (both in alcoholic solution). It therefore seems not improbable that the two oximes have a different structure. In harmony with this conclusion is the fact that camphoroxime is soluble in alkali, whilst α-methylcamphoroxime is insoluble.

Reference may also be made here to the fact that α-methylcamphoroxime undergoes dehydration as readily as camphoroxime itself when heated with dilute sulphuric acid, showing that substitution in the α-position has no marked influence on the readiness with which the nitrile is formed.

In conclusion, mention may be made of what appears to be a case of isomorphism met with in the present investigation.

In an attempt to separate a mixture of camphor and its α-methyl homologue by bromination and subsequent fractional crystallisation of the resulting product, a substance was obtained which, although it melted within a degree of the temperature given by Minguin as the melting point of α′-bromo-α-methylcamphor, on analysis was found to contain more bromine than was required by theory. Subsequently, it was shown to be a mixture of αα′-dibromo- and α′-bromo-α-methylcamphor, which remained practically constant in composition notwithstanding repeated crystallisation.

That the two compounds are in all probability isomorphous follows from the fact that they both crystallise in the orthorhombic system and have the axial ratios:

αα′-Dibromocamphor	1·5778 : 1 : 2·0685	(Zepharovitch, *Monatsh.*, 1882, **3**, 231).
α′-Bromo-α-methylcamphor......	0·7604 : 1 : 0·4921	(Minguin, *Compt. rend.*, 1903, **136**, 752).

Multiplying *a* by 2 and *c* by 4, we obtain the axial ratios for the latter compound: 1·5208 : 1 : 1·9684.

It seems therefore that α′-bromo-α-methylcamphor belongs to the isomorphous series the existence of which was first pointed out by Lowry (Trans., 1898, **73**, 574):

αα′-Dibromocamphor....................	1·5778 : 1 : 2·0685
α′-Chloro-α-bromocamphor	1·5395 : 1 : 1·9144
α-Chloro-α′-bromocamphor	1·5338 : 1 : 1·9020
αα′-Dichlorocamphor	1·4820 : 1 : 1·8358
α′-Bromo-α-methylcamphor............	[1·5208 : 1 : 1·9684]

EXPERIMENTAL.

α-Methylcamphor was first prepared by Minguin (*Compt. rend.*, 1891, **112**, 1370) from methyl α-methylcamphor-α′-carboxylate. Since this method of preparation, commencing with camphor, necessitates the preparation of three intermediate compounds, attempts were made at the beginning of the investigation to synthesise this compound directly from camphor by acting on the sodium derivative of the latter with methyl iodide.

Finely-powdered sodamide was added to a solution of camphor in dry benzene in a flask fitted with a reflux condenser and the mixture heated until ammonia ceased to be evolved; methyl iodide was then added very cautiously to the sodium camphor so obtained and the whole heated for some time; the product was shaken several times with water to remove the sodium bromide and then repeatedly extracted with a mixture of four parts of concentrated sulphuric acid with one part of water. On pouring the acid extract into water, an oil was precipitated; this was separated by steam distillation from the acid liquid, dried, and fractionally distilled. The chief fraction passed over between 215—218°; it solidified after some time at about 10°.

Since α-methylcamphor boils at 220°, it was evident that this fraction was not pure α-methylcamphor but probably a mixture of this compound with unchanged camphor. As it was impossible by mere fractional distillation to effect a separation of the two substances, it was decided to brominate the mixture and submit the product to fractional crystallisation so as to obtain α′-bromo-α-methylcamphor, from which pure α-methylcamphor could be prepared by treatment with zinc dust in alcoholic solution.

The fraction boiling at 215—218° was therefore heated in a flask on a water-bath and bromine added, drop by drop, slightly in excess of the quantity required by theory. The mixture having been heated until hydrogen bromide ceased to be evolved was shaken with a dilute solution of sodium hydroxide and the pasty mass so obtained fractionally distilled in steam. The solid product was purified by crystallisation from alcohol and then from light petroleum, from which solvent it crystallised in large prisms melting at 62°. It was at first thought that this product was α′-bromo-α-methylcamphor, which according to Minguin (*Compt. rend.*, 1903, **136**, 752) melts at 61°. However, on analysis, this was found not to be the case:

I. 0·2303 gave 0·1986 AgBr. Br = 36·70.
II. 0·1768 ,, 0·1524 AgBr. Br = 36·68.
$C_{11}H_{17}OBr$ requires Br = 32·65 per cent.

The substance was then recrystallised three times from light petroleum and again analysed:

I. 0·1871 gave 0·1621 AgBr. Br = 36·87.
II. 0·1790 ,, 0·1550 AgBr. Br = 36·85.

From these results, it is clear that the composition of the substance had undergone no change during the recrystallisation. The observed rotation of an ethyl-alcoholic solution containing 0·7542 gram per 15 c.c. of solution in a 2-dcm. tube at 20° was +14·64°, whence

$[\alpha]_D^{20}$ +145·4°. The specific rotatory power of α′-bromo-α-methylcamphor is $[\alpha]_D^{20}$ +184·4°. Now if the substance were an impure α′-bromo-α-methylcamphor, it follows from these figures that the impurity must have been one containing more bromine and of smaller specific rotatory power than this compound. Since αα′-dibromocamphor melts at 61° and has the specific rotatory power $[\alpha]_D$ +40°, it was thought probable that the impurity might be αα′-dibromocamphor. Some of the substance was therefore mixed with a little αα′-dibromocamphor and the melting point of the mixture determined; it was found to be 61°. This result tends to show the correctness of the conclusion; it may here be mentioned that subsequently, when the substance containing 36·7 per cent. of bromine was heated with a large excess of alcoholic potash, not only was methylenecamphor obtained but also α-bromocamphor, m. p. 76°, derived from the αα′-dibromocamphor present. An attempt was made to obtain pure α′-bromo-α-methylcamphor from the mixture by treatment with small quantities of alcoholic potash, the object being to convert the αα′-dibromocamphor into α-bromocamphor and by fractional crystallisation to separate this compound from the α′-bromo-α-methylcamphor; but this was not a success.

Hydrolysis of Methyl α-Methylcamphor-α′-carboxylate.

Since pure α-methylcamphor could not be obtained directly from camphor, it was prepared by hydrolysing methyl α-methylcamphor-α′-carboxylate. Brühl (*Ber.*, 1902, **35**, 3622) has shown that when a mixture of this ester with five times its weight of 15 per cent. sodium methoxide in methyl alcohol is heated for about four hours at 80°, it is completely hydrolysed, α-methylcamphor-α′-carboxylic acid being formed together with some α-methylcamphor. It seemed probable, therefore, that a complete conversion into α-methylcamphor would be effected by prolonged heating, and that the rather objectionable method originally used by Minguin, namely, treatment of the ester with alcoholic potash in sealed tube at 120—130° for twelve hours, might be dispensed with. However, it was found that even after heating the ester with sodium methoxide on a water-bath during twenty-four hours only about one-half had been converted into α-methylcamphor, so it was decided to use alcoholic potash as the hydrolysing agent and an autoclave instead of sealed tubes.

A flask containing 110 grams of the ester dissolved in about 400 c.c. of 95 per cent. ethyl alcohol, to which had been added a solution of 60 grams of potassium hydroxide in 50 c.c. of water, was placed in an autoclave; this was heated in an oil-bath the temperature of which was maintained at 160—170° during about twelve hours. The liquid in the flask was then poured into a fairly large quantity of water, the α-methylcamphor was extracted with ether and the ethereal solution dried and fractionally distilled. At first ether and alcohol passed over, after which were obtained the following fractions: I. 216—220° = 16 grams. II. 222—223° = 26 grams. III. 223—233 = 15·5 grams. Refractionation yielded a fraction boiling at 220—221°, which solidified on cooling to a crystalline solid melting at 37—38, the temperature given by Minguin. Further purification may be effected by diluting a 5 per cent. alcoholic solution with a moderately large bulk of water; the α-methylcamphor separates from the diluted alcohol in white, glistening leaflets melting at 38—39°. An ethyl-alcoholic solution of the compound containing 5 grams per 100 c.c. of solution gave $[\alpha]_D^{25}$ + 30·0°. Minguin in his first communication on α-methylcamphor (*Compt. rend.*, 1891, **112**, 1370) gives $[\alpha]_D$ + 270·65° (1·66 grams per 10 c.c.), which value is that quoted in all text-books. Subsequently (*Compt. rend.*, 1903, **136**, 752) he gives the value $[\alpha]_D$ + 27·65°. The addition of sodium ethoxide to the alcoholic solution of α-methylcamphor is unaccompanied by any change in the specific rotatory power of the solution, so that, although still containing a hydrogen atom in the α-position, α-methylcamphor is apparently not converted into its stereoisomeride under the influence of sodium ethoxide.

α′-Bromo-α-methylcamphor.

This compound, originally obtained by Minguin by treating α-methylcamphor dissolved in carbon disulphide with bromine, is more readily prepared by gradually adding the theoretical quantity of bromine to the alkylcamphor contained in a flask heated on a water-bath. When hydrogen bromide ceases to be evolved, the crude product is washed with dilute sodium hydroxide and recrystallised several times from hot alcohol, from which it separates in crystals melting at 62·5° (Minguin gives 61°) and resembling ammonium chloride. A mixture of four parts of this compound with one part of αα′-dibromocamphor (m. p. 61°) was found to melt at 60—61·5°, so that the conclusion arrived at above with reference to the compound obtained by the bromination of the mixture of camphor and α-methylcamphor receives additional support:

0·1864 gave 0·1438 AgBr; Br = 32·82.
0·1510 ,, 0·1154 AgBr; Br = 32·52.
$C_{11}H_{17}OBr$ requires Br = 32·65 per cent.

The specific rotatory power was determined in 99·5 per cent. ethyl-alcoholic solution, the concentration being 5 grams per 100 c.c.; the value obtained was $[\alpha]_D^{20}$ + 184·4° (Minguin gives $[\alpha]_D$ + 176·8°). The specific rotatory power twenty hours after the addition of sodium ethoxide to make the solution approximately *N*/1000 was

$[\alpha]_D^{20}$ +184·1°; in other words, *a*′-bromo-*a*-methylcamphor undergoes no stereoisomeric change in the presence of traces of sodium ethoxide. Similarly, a benzene solution containing 0·6966 gram per 15 c.c. of solution was examined in a 2-dcm. tube at 25°. The rotation observed was +17·73°, whence $[\alpha]_D^{25}$ +190·8°. One drop of piperidine was then added to the contents of the tube; the rotation observed twenty-four hours after the addition of the base was +17·70°, so that no isomeric change had been produced by the presence of this base.

ω-Bromo-a-methylcamphor.

This isomeride of the compound just described is prepared by the addition of hydrogen bromide to methylenecamphor. The latter compound is obtained by boiling for sixteen hours a solution of 30 grams of *a*′-bromo-*a*-methylcamphor in 140 c.c. of alcohol with 30 grams of potassium hydroxide dissolved in an equal weight of water. The brown solution thus obtained is diluted with water, distilled in steam, the distillate extracted with ether, and the ethereal solution dried and then fractionally distilled. The portion which passes over between 216° and 219° (10 grams) is practically pure methylenecamphor.

In order to bring about the interaction of hydrogen bromide and methylenecamphor, the latter compound is dissolved in about three times its weight of a cold saturated solution of hydrogen bromide in glacial acetic acid and the mixture allowed to stand in a stoppered bottle at the ordinary temperature for at least six weeks. At the end of this period, the light brown solution is diluted with a large volume of water, the heavy oil which separates is washed with dilute sodium hydroxide and the pasty mass so obtained washed thoroughly with water and dried on a porous plate. The crude product is best purified by crystallisation from alcohol, from which solvent it crystallises in colourless prisms melting at 65—66°:

0·1444 gave 0·1116 AgBr. Br = 32·88.
0·1734 „ 0·1330 AgBr. Br = 32·64.
$C_{11}H_{17}OBr$ requires Br = 32·65 per cent.

The specific rotatory power was determined in 99·5 per cent. ethyl-alcoholic solution containing 5 grams per 100 c.c. The value obtained was $[\alpha]_D^{20}$ +155·4°: Minguin gives $[\alpha]_D$ +150·5°.

The specific rotatory power twenty hours after the addition of sodium ethoxide to render the solution approximately *N*/1000 was $[\alpha]_D^{20}$ +155·2°, so that this compound also appears to undergo no stereoisomeric change in the presence of sodium ethoxide. With the object of confirming this result, a benzene solution containing 0·57 gram per 15 c.c. of solution was examined in a 2-dcm. tube at 25°. The rotation observed was +10·08°, whence $[\alpha]_D^{25}$ +132·6°. One hour after the addition of a drop of piperidine to the contents of the tube, the observed rotation was +10·1°; the rotation twenty-four hours after the addition of the base could not be accurately determined, owing to the separation of fine needle-shaped crystals of piperidine hydrobromide; however, no very marked change in the rotatory power could be detected.

The fact that the addition of alkali to the solution had no effect on the optical rotatory power seemed to support the suggestion that this compound is an α′-bromo-α-methylcamphor; in other words, a stereoisomeride of the compound melting at 62·5°. Further investigation, however, proved this to be incorrect.

Action of Potassium Permanganate and Nitric Acid on the Isomeric Monobromo-derivatives of α-Methylcamphor.

The two isomerides were treated under exactly identical conditions with equal volumes of an aqueous solution of potassium permanganate; although both remained practically unaffected by this agent even after very prolonged heating, nevertheless it was observed that the colour of the permanganate was discharged quicker and more bromide was found in solution in the case of the isomeride melting at 65—66° than in that melting at 62·5°.

A still greater difference was observed in the behaviour of these substances towards concentrated nitric acid (sp. gr. 1·42). When the isomeride melting at 62·5° is added to nitric acid containing in suspension some finely-divided silver nitrate, it at once becomes oily and almost immediately a dense, yellow precipitate of silver bromide appears the quantity of which increases considerably on standing. On the other hand, the isomeride melting at 65—66° does not give a precipitate of silver bromide when similarly treated and may be recovered unchanged even after standing some days in contact with the acid. This result tends to confirm Minguin's conclusions, since it is to be expected that α′-bromo-α-methylcamphor melting at 62·5° would lose bromine more readily than ω-bromo-α-methylcamphor melting at 65—66°.

A yellow oil slightly denser than water was obtained by steam distillation from the product of the interaction of α′-bromo-α-methylcamphor and nitric acid; as the quantity was small, it was not further investigated; it was in all probability an α′-nitro-α-methylcamphor.

Action of Bromine on the Isomerides. Preparation of ω-α′-Dibromo-α-methylcamphor, $C_{10}H_{14}Br(CH_2Br)O$.

When a mixture in equimolecular proportions of the compound melting at 65—66° and bromine is heated on a water-bath, hydrogen bromide is evolved, the mixture becoming almost colourless. The crude substance thus obtained, after washing with dilute sodium hydroxide and finally with water, is readily purified by crystallisation from hot alcohol, from which solvent it is obtained in long, slender, colourless, silky needles melting at 108—109°. The compound thus formed is a dibromo-derivative of α-methylcamphor:

0·1430 gave 0·1663 AgBr. Br = 49·49.
0·1604 „ 0·1865 AgBr. Br = 49·48.
$C_{11}H_{16}OBr_2$ requires Br = 49·35 per cent.

When similarly treated with bromine, the isomeride melting at 62·5° remains unattacked; there is therefore little doubt that this compound is α'-bromo-α-methylcamphor, whilst the isomeride melting at 65—66° is ω-bromo-α-methylcamphor.

That the above dibromo-derivative of α-methylcamphor is undoubtedly ω-α'-dibromo-α-methylcamphor follows from the fact that the same compound is produced by the addition of bromine to methylenecamphor. When the latter compound is mixed with the theoretical quantity of bromine, it is at once evident that interaction has taken place, since heat is generated and the colour of the halogen slowly disappears. After two or three crystallisations from hot spirit, the product melts at 108°; a mixture of this substance with that obtained by brominating ω-bromo-α-methylcamphor melts at 108°.

ω-α'-Dibromo-α-methylcamphor is only moderately soluble in cold alcohol or light petroleum but is readily so in benzene, from which it crystallises in stout, colourless prisms.

For the determination of the rotatory power, a benzene solution containing 0·715 gram per 15 c.c. of solution was examined in a 2-dcm. tube at 20°. The rotation observed was +11·203°, whence $[\alpha]_D^{20}$ +117·5°.

α-Methylcamphor-β-sulphonic Acid.

This acid is obtained quite readily from α-methylcamphor by the method originally described by Reychler (*Bull. Soc. chim.*, 1898, **19**, [iii], 120). A mixture of acetic anhydride and sulphuric acid is prepared by cautiously adding two parts by weight of the latter compound to four parts by weight of the former and to the mixture is added three parts of α-methylcamphor. The slightly brown solution, after standing several days in the cold, deposits large, transparent crystals of the sulphonic acid; if, however, a little of the solid acid be added to the mixture even after standing only twenty-four hours, a copious separation of the sulphonic acid at once takes place. When no more sulphonic acid separates out, the liquid is allowed to drain away from the crystalline mass, which is then washed two or three times with small quantities of glacial acetic acid and finally purified by recrystallisation from hot ethyl acetate. The sulphonic acid remaining in the acid mother-liquor may be separated by boiling the diluted mixture several hours with animal charcoal until practically the whole of the acetic acid has been volatilised, when the liquid is filtered and neutralised with barium carbonate. The barium salt separates from the filtered solution when sufficiently concentrated and is best purified by recrystallisation from water.

a-Methylcamphor-β-sulphonic acid crystallises from hot ethyl acetate in large, transparent prisms, which quickly become opaque when removed from the solution. It is an exceedingly deliquescent substance, which melts at 114—116° but is decomposed; it dissolves readily in cold water and hot glacial acetic acid or ethyl acetate. The observed rotatory power of an aqueous solution containing 0·7608 gram per 15 c.c. of solution in a 2-dcm. tube at 20° was +1·897°, whence $[\alpha]_D^{20}$ +18·7°.

Barium a-methylcamphor-β-sulphonate, $(C_{11}H_{17}O_4S)_2Ba,6H_2O$, crystallises from hot aqueous solutions of suitable concentration in large, stout, transparent, hexagonal plates, which melt in their water of crystallisation at 66°. The salt parts with the whole of its water of crystallisation when kept in a desiccator over concentrated sulphuric acid for two or three days:

0·5740 gave 0·1770 $BaSO_4$. Ba = 18·15. 0·4950 gave 0·1536 $BaSO_4$. Ba = 18·26. 0·5628 gave 0·1740 $BaSO_4$. Ba = 18·20.

0·4260 lost 0·0626 H_2O. H_2O = 14·69. 0·5982 lost 0·0889 H_2O. H_2O = 14·86. 0·4954 lost 0·0750 H_2O. H_2O = 15·13.

$(C_{11}H_{17}O_4S)_2Ba,6H_2O$ requires Ba = 18·68; H_2O = 14·69 per cent.

The *potassium* salt could not be obtained in a crystalline form; an aqueous solution evaporated on a water-bath leaves a somewhat gelatinous residue, which becomes quite hard and brittle on standing a few days in a vacuum desiccator over sulphuric acid.

a-Methylcamphor-β-sulphonyl chloride, $C_{11}H_{17}O\cdot SO_2Cl$, is prepared by rubbing together phosphorus pentachloride and a slight excess of the anhydrous potassium sulphonate. The semi-solid mixture is allowed to stand for two or three hours and then poured on to, and intimately ground up with, a large quantity of finely-powdered ice, after which the solid sulphonyl chloride is collected, washed well with ice-water, and dried in a vacuum desiccator. The crude substance is purified by crystallisation from light petroleum at temperatures below 10°:

0·1972 gave 0·1054 AgCl. Cl = 13·20.
0·3366 „ 0·1798 AgCl. Cl = 13·19.

$C_{11}H_{17}O_3ClS$ requires Cl = 13·39 per cent.

The sulphonyl chloride crystallises in transparent, prismatic needles, which melt at 33°; it is a fairly stable substance which is readily dissolved by most organic solvents. The observed rotation of a 5 per cent. solution in benzene in a 2-dcm. tube was $+2{\cdot}95°$, whence $[a]_D^{20}$ $+29{\cdot}5°$.

a-Methylcamphor-β-sulphonamide, $C_{11}H_{17}O{\cdot}SO_2{\cdot}NH_2$, is obtained when the sulphonyl chloride is treated with a concentrated aqueous solution of ammonia. To separate it from any anhydramide which may possibly be formed at the same time, it was crystallised twice from hot water—in which the anhydramide is only very sparingly soluble—and finally from either hot alcohol or benzene:

0·2372 gave 11·65 c.c. N_2 (dry) at 12·5° and 756 mm. N = 5·86.
0·1898 " 9·35 c.c. " " 13·5° " 749·2 mm. N = 5·80.
$C_{11}H_{19}O_3NS$ requires N = 5·72 per cent.

The sulphonamide crystallises from hot water in long, silky needles, and from hot alcohol in transparent prisms, which melt at 150°. Unlike camphor-β-sulphonamide, it does not lose water when heated above its melting point and may even be heated to 200° without undergoing decomposition.

The observed rotation effected by a chloroform solution containing 0·376 gram per 15 c.c. of solution in a 2-dcm. tube at 20° was $-0{\cdot}316°$, whence $[a]_D^{20}$ $-6{\cdot}3°$.

a-Methylcamphor-β-sulphonanhydramide.—As was first observed by Lowry (Trans, 1902, **81**, 1448), camphor-β-sulphonamide when covered with a concentrated solution of hydrogen chloride quickly dissolves and in a few minutes the anhydramide separates from the solution. The behaviour of *a*-methylcamphor-β-sulphonamide towards the acid is somewhat similar, although in this case it is necessary to heat the acid in order to dissolve the sulphonamide.

The anhydramide separates very slowly from the solution so obtained on standing:

0·1918 gave 10 c.c. N_2 (dry) at 17° and 754·2 mm. N = 6·11.
0·1900 " 10·1 c.c. " " 15° " 746 mm. N = 6·20.
$C_{11}H_{15}O_2NS$ requires N = 6·16 per cent.

The anhydramide is practically insoluble in cold water and alcohol, sparingly soluble in hot alcohol. It separates from a solution in hot alcohol as a fine crystalline powder, which melts at 167·5°.

β-Bromo-a-methylcamphor, $C_{11}H_{17}OBr$, is formed when *a*-methylcamphor-β-sulphonyl bromide is heated, sulphur dioxide being simultaneously evolved. The *sulphonyl bromide*, prepared by the interaction of phosphorus pentabromide and the anhydrous potassium sulphonate, could not be obtained in the solid state, so the oily substance was dissolved in dry xylene and the solution boiled in a flask, fitted with a reflux condenser, for about twelve hours. At the end of this period, sulphur dioxide had ceased to be evolved, so the resulting solution of β-bromo-a-methylcamphor was submitted to fractional steam distillation. At first, practically only xylene passed over with the water vapour but towards the end of the distillation an oil passed over which was heavier than water. On standing, traces of xylene present in the oil evaporated off and left a solid which crystallised from dilute alcohol in silky needles melting at 55° :

0·1180 gave 0·0908 AgBr. Br = 32·74.

$C_{11}H_{17}OBr$ requires Br = 32·65 per cent.

The observed rotation effected by an ethyl-alcoholic solution containing 0·2586 gram per 15 c.c. of solution in a 2-dcm. tube at 25° was +0·65°, whence $[a]_D^{25} + 18·8°$. The specific rotatory power twenty-four hours after the addition of sodium ethoxide to render the solution approximately *N*/100 was $[a]_D^{25} + 18·0°$. It is therefore evident that β-bromo-a-methylcamphor is not converted into β-bromo-a′-methylcamphor under the influence of sodium ethoxide. β-Bromo-a-methylcamphor is extremely soluble in the common organic solvents.

a-*Methylcamphoroxime*, $C_{11}H_{18}{:}NOH$.

a-Methylcamphor yields an oxime but not quite so readily as camphor. It may be prepared as follows: A solution of 20 grams of hydroxylamine hydrochloride in an equal weight of hot water is added to a solution of 11 grams of a-methylcamphor in 150 c.c. of alcohol and to the mixture is added 12 grams of finely-powdered potassium carbonate. The mixture is kept at the ordinary temperature for a day, then heated to boiling and again kept at the ordinary temperature for several days, after which it is diluted considerably with water and the viscid oil which separates submitted to fractional steam distillation. At first, an oil passes over with the water vapour but after some time a very viscid oil distils over, which solidifies very slowly on standing. This crude material is purified with some difficulty by repeated crystallisation from dilute alcohol (1 : 1), from which it separates in crystals resembling ammonium chloride ; from more dilute alcohol, it crystallises in long, slender needles melting at 55° :

0·2002 gave 13·65 c.c. N_2 (dry) at 23° and 745 mm. N = 7·77.
0·1506 „ 10·3 c.c. „ „ 19° „ 753 mm. N = 7·94.

$C_{11}H_{19}ON$ requires N = 7·73 per cent.

a-*Methylcamphoroxime* possesses a strong camphor-like odour, is extremely soluble in all common organic solvents, but unlike camphoroxime, it does not dissolve in aqueous alkalis.

The specific rotatory power was determined in 99·5 per cent. ethyl-alcoholic solution. The values obtained were $[a]_D^{20}$ +30·3° (5 grams per 100 c.c. of solution) and $[a]_D^{20}$ +32·0° (2·5 grams per 100 c.c. of solution).

The Hydrochloride.—When dry hydrogen chloride is passed into a solution of the oxime in dry ether, a copious precipitate of the *hydrochloride* is obtained in silky needles. It melts but undergoes decomposition at 138° and is hydrolysed by water:

0·1692 required 7·45 c.c. of *N*/10 KOH. HCl = 16·05.

$C_{11}H_{20}ONCl$ requires HCl = 16·75 per cent.

α-Methylcamphoroxime dissolves in warm dilute sulphuric acid, forming a clear solution, which, however, when heated to boiling, quickly becomes turbid, owing to the separation of a pleasant smelling oil. This was separated from the dilute acid by steam distillation, dried and fractionally distilled. The principal fraction, which passes over between 226° and 228°, is a colourless oil possessing a somewhat peppermint-like odour. From its mode of formation, it is in all probability *methylcampholenonitrile*, produced by the dehydration of the oxime by the dilute sulphuric acid, since, when boiled with alcoholic potash, ammonia is slowly evolved. The acid formed by the hydrolysis of the nitrile has not yet been investigated.

In conclusion, the author desires to express his thanks to Professor H. E. Armstrong for suggesting this work, and for the valuable advice he has given him in carrying it out.

CHEMICAL DEPARTMENT, CITY AND GUILDS OF LONDON INSTITUTE,
CENTRAL TECHNICAL COLLEGE.

CXXIV.—*Viscosity Determinations at High Temperatures.*

By CHARLES EDWARD FAWSITT.

THE experimental determination of the viscosity of liquids at high temperatures constitutes rather a difficult problem. That this subject should have been so much avoided hitherto is to be regretted, as, apart from the stoicheiometrical relations involved, the bearing of this property on crystallisation deserves close examination. In the present communication the results from the examination of some fused salts and metals are submitted.

A few determinations of viscosity at high temperatures have already been carried out. Koch (*Wied. Annalen*, 1881, **14**, 1) has determined the viscosity of mercury over a large range of temperature. Beck (*Zeitsch. physikal. Chem.*, 1907, **58**, 425) has determined the viscosity of mercuric bromide and iodide. Lorenz and Kalmus (*Zeitsch. physikal. Chem.*, 1907, **59**, 244) have determined the viscosity of five fused salts. Goodwin and Mailey (*Phys. Review*, 1908, **26**, 28) have worked on the viscosity of a number of nitrates, and have also determined their electrical conductivities. All these results are confined to temperatures below 600°, and the experimenters were able to use the capillary method in all cases. Some interesting measurements at higher temperatures have been made on silicates by Doelter (*Sitzungsber. K. Akad. Wien*, 1905, **114**, 529), and Arndt (*Zeitsch. Elektrochem.*, 1907, **13**, 578) has determined the viscosity of sodium metaphosphate and boric anhydride. The two last-named experimenters have worked with liquids of very high viscosity, and their methods of experiment are of no use for the determination of the viscosity of fused metals or of the majority of salts, as these have a relatively low viscosity.

Method.—In a communication recently published (*Proc. Roy. Soc.*, 1908, **80**, *A*, 290) the author has given a general description of a method devised more especially for the determination of the viscosity of fused metals and salts. In this method a small disk of iron, platinum, or fireclay is allowed to oscillate torsionally in the liquid, the viscosity of which is to be determined. From the observations it is possible to calculate the logarithmic decrement of the amplitude, and from this the viscosity of the liquid, provided its density is known. The apparatus is standardised in three liquids of known viscosity and density. Having standardised the apparatus, it is advisable to test it in a further number of liquids of known viscosity in order to find what degree of accuracy is obtainable. It was found that with a disk of 26—29 mm. diameter, the accuracy obtainable could be taken as ±2 per cent. In using the disk at high temperatures, a small correction for its expansion is made. The disk is attached at its centre to a thin rod, which at its upper end is attached to a copper suspension wire. The wire used in these experiments was about one metre long, and the period of oscillation of the apparatus about eight seconds. The period was practically identical in all the liquids examined. The apparatus was first of all allowed to swing in air and the logarithmic decrement noted. It was then allowed to swing in the three standardising liquids. These should be chosen so that one at least of them has a viscosity and density near to the viscosity and density of the liquid, the viscosity of which is to be determined. When working with salts, the three liquids used were water, chloroform, and fused sodium nitrate. When working with metals, mercury, chloroform, and *iso*butyl alcohol were taken.

Whilst this method appears at first sight to have great simplicity, its application is nevertheless attended with some difficulties. The difficulties are due to errors caused by impurities on the surface of the liquid. When the disk is allowed to sink into the liquid, the only part of the apparatus which comes in contact with the surface is the relatively thin stem. The diameter of the stem was 2 mm., and it might be imagined that the impeding action of any surface impurity on this would be so slight as to be negligible. That is, however, not so; the surface of any liquid, and more especially the surface of a metal (even if non-oxidisable), is liable to have its surface skin rendered very viscous, although no visible impurity is present. The cause of this is undoubtedly the presence of some dust or dirt in an amount too small to be visible. The errors caused by such impurities easily amount to 10 per cent. When any visible impurity is present on the surface, experiment is hopeless. When every care is taken to prepare mercury pure and clean, the surface skin is not any more viscous than any layer in the interior. But if it be allowed simply to stand, it will soon become much more viscous. The most satisfactory method of experiment with mercury or any other metal is to cover the surface with another liquid. In the case of mercury, it will be found that a thin layer of very dilute nitric acid keeps the surface in good condition. Below 270° (molten tin), it is possible to get a good, clean surface by covering with melted resin. From 270° upwards for about two hundred degrees, a cover of zinc and ammonium chlorides answers well. At higher temperatures, the only cover which gave any results was borax. Attempts were made to keep the surface of oxidisable metals clean by filtering them and then keeping them in an atmosphere of carbon dioxide; in all cases, however, a very small amount of oxygen leaked in, and this sufficed to spoil the results. It is undoubtedly best to use a cover of some kind.

In the experiments with both metals and salts, a large number of observations were made at each temperature given. As all the errors are in the direction of producing results that are too high, the lowest results have always been considered the correct ones, and the numbers for viscosity given here are the lowest results obtained in each case.

The experiments give the logarithmic decrement of the amplitude, and from this the viscosity is obtained by the formula

$$\lambda - \lambda_0 = c_1 \sqrt{\mu d} + c_2\mu + c_3\mu d,$$

where λ is the logarithmic decrement for the liquid experimented on,

λ_0 is the logarithmic decrement for air,

μ is the viscosity of the liquid, and d its density.

c_1, c_2, c_3 are constants, and are obtained by experimenting with liquids of known viscosity.

The calculations thus involve the solution of three (linear) simultaneous equations and the subsequent solution of a quadratic equation.

The numbers in the density column were obtained in the case of the metals and sodium chloride from Landolt and Börnstein's *Tabellen* (1905). The other numbers were obtained by experiment. The method used was that of sinking a ball of platinum in the fused liquid and noting the consequent loss of weight. Temperature was measured by a platinum and platinum-rhodium thermo-couple connected to a Siemens-Halske galvanometer. The readings may be taken as correct to ± 5°. The viscosities are given in absolute (C.G.S.) units.

Viscosity Measurements on Fused Salts.

These measurements were carried out partly from the interest which attaches to them on their own account, but also because it was tolerably certain that in the case of viscosity, as with other properties, relations obtainable with fused salts would have their parallel in the case of metals. The following salts were examined more particularly: sodium and potassium nitrates, sodium, potassium, and lithium chlorides, and sodium and potassium bromides; also mixtures of sodium nitrate and potassium nitrate. The results are contained in the following tables:

TABLE I.

Sodium Nitrate; m. p. 308°.

Temperature.	Density.	Viscosity.
324°	1·903	0·0271
333	1·899	0·0256
353	1·887	0·0235
393	1·860	0·0200

TABLE II.

Potassium Nitrate; m. p. 339°.

Temperature.	Density.	Viscosity.
349°	1·863	0·0267
362	1·850	0·0240
383	1·833	0·0225
397	1·824	0·0214
407	1·815	0·0200

TABLE III.

Sodium Chloride; m. p. 822°.

Temperature.	Density.	Viscosity.
841°	1·530	0·0130
850	1·520	0·0120
896	1·500	0·0101
924	1·486	0·0097

TABLE IV.

Potassium Chloride; m. p. 782°.

Temperature.	Density.	Viscosity.
790°	1·520	0·0142
835	1·490	0·0121
920	1·438	0·0099
1035	1·370	0·0071

TABLE V.

Sodium Bromide; m. p. 757°.

Temperature.	Density.	Viscosity.
762°	2·324	0·0142
766	2·316	0·0135
780	2·308	0·0128
880	2·220	0·0109

TABLE VI.

Potassium Bromide; m. p. 744°.

Temperature.	Density.	Viscosity.
745°	2·110	0·0148
775	2·087	0·0134
805	2·063	0·0119
862	2·023	0·0105

TABLE VII.

Lithium Chloride; m. p. 605°.

Temperature.	Density.	Viscosity.
617°	1·475	0·0181
645	1·462	0·0164
675	1·450	0·0149
742	1·426	0·0125
765	1·417	0·0114

The results for sodium nitrate, potassium and lithium chlorides, and potassium bromide are plotted in Fig. 1. If the salts are compared at temperatures 20° above the respective melting points, the following results are obtained:

FIG. 1.

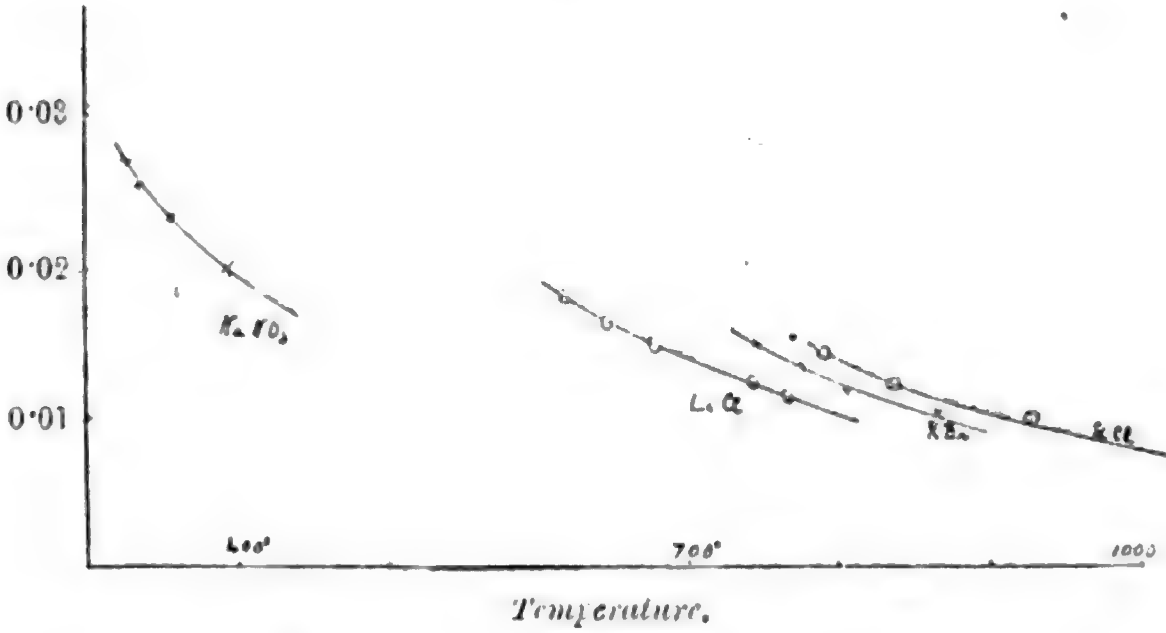


TABLE VIII.

Substance.	Temperature.	Viscosity.
$NaNO_3$	328°	0·0262
KNO_3	359	0·0251
NaCl	842	0·0128
KCl	802	0·0133
NaBr	777	0·0130
KBr	764	0·0137
LiCl	625	0·0176

The first thing noticeable about these results is that the substances have a relatively small viscosity; the viscosity of water at 20° is 0·0102. Secondly, it will be noticed that the viscosities of the potassium and sodium salts are nearly the same in each case. The lithium salt is noticeably more viscous than the corresponding potassium salt. Goodwin and Mailey (*loc. cit.*) found that lithium nitrate was more viscous than potassium nitrate. Some other salts were examined besides those reported. Zinc chloride and borax, for example, were found to be very viscous, of the same order of viscosity as rape oil. These, however, are undoubtedly exceptional; and it appears that the majority of fused salts have a small viscosity.

Mixtures of Salts.

Mixtures of sodium and potassium nitrates were examined, and the observations in all cases were continued to as near the melting point as possible. The proportions in the mixtures are expressed in percentage by weight.

TABLE IX.

Sodium Nitrate (80) *and Potassium Nitrate* (20); m. p. 278°.

Temperature.	Density.	Viscosity.
278°	1·930	0·0325
328	1·894	0·0248
344	1·884	0·0234
373	1·864	0·0217

TABLE X.

Sodium Nitrate (60) *and Potassium Nitrate* (40); m. p. 240°.

Temperature.	Density.	Viscosity.
262°	1·938	0·0368
276	1·928	0·0324
316	1·897	0·0247
332	1·883	0·0237

TABLE XI.

Sodium Nitrate (45·5) *and Potassium Nitrate* (54·5); m. p. 224°.

Temperature.	Density.	Viscosity.
229°	1·963	0·0470
236	1·957	0·0446
269	1·934	0·0334
286	1·920	0·0296
291	1·916	0·0287
309	1·902	0·0266
331	1·884	0·0247
346	1·873	0·0238

TABLE XII.

Sodium Nitrate (35) *and Potassium Nitrate* (65); m. p. 237°.

Temperature.	Density.	Viscosity.
245°	1·943	0·0423
253	1·936	0·0405
289	1·907	0·0306
340	1·870	0·0246

TABLE XIII.

Sodium Nitrate (24) *and Potassium Nitrate* (76); m. p. 263°.

Temperature.	Density.	Viscosity.
276°	1·920	0·0338
326	1·880	0·0259
335	1·873	0·0242

The melting-point curve for mixtures of sodium and potassium nitrates has already been studied by Carveth (*J. Physical Chem.*, 1898, **2**, 209), and the eutectic point was found to exist at the composition 45·5 per cent. of sodium nitrate and 54·5 per cent. of potassium nitrate. If the viscosities of the mixtures at temperatures 20° above the melting points are taken for comparison, the following numbers are obtained:

TABLE XIV.

Composition per cent. NaNO$_3$.	Composition per cent. KNO$_3$.	Temperature.	Viscosity.
100	0	328°	0·0262
80	20	298	0·0287
60	40	260	0·0370
45·5	54·5	244	0·0410
35	65	257	0·0387
24	76	283	0·0322
0	100	359	0·0250

These results are shown graphically in Fig. 2.

There is a distinct maximum at the composition represented by the eutectic mixture.

It is also of interest here to consider the viscosities at temperatures linearly situated between 308° and 339°, the melting points of the (pure) components. As the viscosities of sodium nitrate and potassium nitrate at their melting points are almost the same, it might be expected that the viscosities of all the mixtures would also be the same if compared at temperatures linearly situated between the melting points of the components.

FIG. 2.

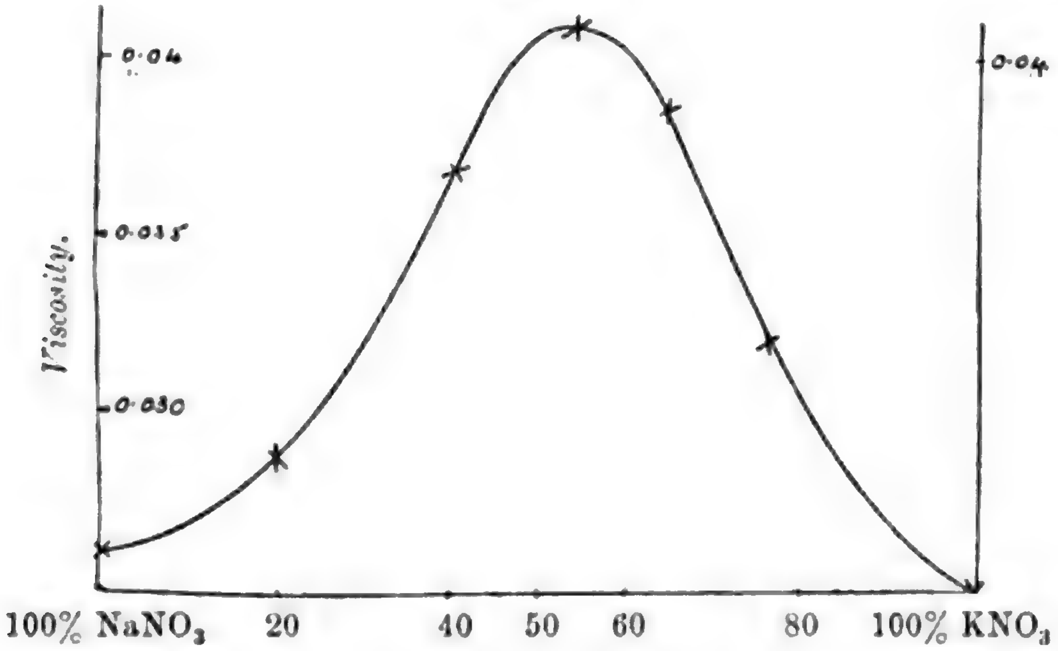


TABLE XV.

Composition per cent. NaNO$_3$.	Composition per cent. KNO$_3$.	Temperature.	Viscosity.
100	0	308°	0·0296
80	20	314	0·0266
60	40	320	0·0244
45·5	54·5	324	0·0252
35	65	327	0·0255
24	76	331	0·0250
0	100	339	0·0283

There is a distinct decrease in the viscosity when the two salts are mixed. The fall is probably connected with a change in the dissociation caused by the mixing of the salts.

The Variation of Viscosity with Temperature.

The viscosity of a salt diminishes with rising temperature; the change is more rapid at first than afterwards. Comparing different salts, it will be noticed that those which have the greater viscosity at their melting points are also those whose viscosity falls most rapidly with rising temperature. This matter may be best discussed by considering in each case the fall of viscosity for equal intervals of temperature measured from the melting point, or a temperature equally distant from the melting point. Take, for example, in each case, the viscosity at 20° and at 70° above the melting point; let these be denoted by μ_{20} and μ_{70} respectively; let μ_a be the average viscosity throughout the interval. Then $\frac{\mu_{70}-\mu_{20}}{\mu_a}$, which is proportional to the temperature coefficient, should be a comparable function for different salts.

In the following table, the values of $\frac{\mu_{70}-\mu_{20}}{\mu_a}$ for a number of the substances are given, also the quotients of this function by μ_a.

TABLE XVI.

Substance.	μ_a.	$\frac{\mu_{70}-\mu_{20}}{\mu_a}$.	$\frac{\mu_{70}-\mu_{20}}{(\mu_a)^2}$.
KNO_3	0·0226	0·212	9·4
$NaNO_3$	0·0236	0·220	9·3
45·5% $NaNO_3$ and 54·5% KNO_3	0·0345	0·377	10·9
KCl	0·0125	0·128	10·3
KBr	0·0126	0·143	11·3
LiCl	0·0162	0·173	10·7

The numbers in the last column are remarkably close to each other, thus showing that for these substances the temperature coefficient of the viscosity of a salt is very nearly proportional to its viscosity.

The Viscosity of Metals.

Experiments were tried with copper, zinc, lead, tin, bismuth, cadmium, and mercury. It was found that the viscosity values were much lower than had been expected. Metals are, in fact, of the same order of viscosity as the salts just examined. Considerable difficulty has so far been experienced in obtaining trustworthy numbers for the metals, and in the meantime the only figures given are such as could easily be repeated with the same result. These numbers were obtained from mercury, tin, lead, bismuth.

TABLE XVII.

Substance.	Temperature.	Density.	Viscosity.
Mercury	65°	13·43	0·0138
	95	13·39	0·0124
	133	13·27	0·0116
	216	13·08	0·0106
Tin (m. p. 232°)	234	7·00	0·0275
	267	6·98	0·0235
Lead (m. p. 327°)	330	10·65	0·0320
	347	10·63	0·0293
Bismuth (m. p. 270°)	360	9·91	0·0167

If these metals are compared at temperatures equally above their melting points, it is seen that lead is more viscous than tin, tin than bismuth, and bismuth than mercury. But they are closer to one another than would probably have been anticipated.

An important fact which has been noticed is that the viscosity of a metal does not increase in any abrupt manner as the temperature is lowered until it is actually solid. In many cases experiments were carried out with the metal in the crucible half solidified (round the sides), and no difference in viscosity could be detected between this temperature and a temperature a few degrees above this when all was fluid.

Conclusions.

1. The viscosity of many salts and metals is relatively small, being only a few times that of water.
2. The viscosities of sodium and potassium salts of the same acid are nearly the same.
3. Viscosity diminishes with rising temperature. The temperature coefficients for the salts examined vary directly as their viscosities.
4. A eutectic mixture at its melting point has a greater viscosity than the components have at their melting points.

I am much indebted to the Carnegie Trust for the Scottish Universities and to the Chemical Society for grants in aid of this research.

THE UNIVERSITY,
GLASGOW.

CXXV.—*The Formation of Polyiodides in Nitrobenzene Solution. Part III. The Chemical Dissociation of the Polyiodides of the Alkali Metals and Ammonium Radicles.*

By Harry Medforth Dawson.

In a previous paper (Part I, Dawson and Gawler, Trans., 1902, **81**, 524) it has been shown that potassium iodide is readily soluble in nitrobenzene in presence of iodine. Solubility measurements indicated that dilute solutions, saturated with potassium iodide, contain one mol. of iodide per mol. of iodine, whereas solutions saturated with iodine contain four mols. of iodine per mol. of iodide. It is evident that the conditions obtaining in the two series of experiments—saturation with respect to iodide in the one case and with respect to iodine in the other—are such as might be expected to yield information relative to the lowest and highest types of polyiodides respectively, and the experimental data led the authors to conclude that the chief constituents of the two series of solutions are the tri-iodide and the ennea-iodide.

Dawson and Goodson (Part II, Trans., 1904, **85**, 796) have shown that polyiodides of these types are also formed in nitrobenzene under the same conditions by the other alkali metals, the alkaline earth metals, and by ammonium and the substituted ammonium radicles. That polyiodides of the types MI_3 and MI_9 are also formed in certain other solvents has been shown to be probable (Dawson, Trans., 1904, **85**, 467), although, in general, the polyiodides are not so sharply defined in these solutions as they are when nitrobenzene is the solvent. Several factors contribute to this circumstance, so far as the experimental investigation of the polyiodides is concerned. In the first place, the polyiodides are, in general, readily soluble in nitrobenzene, whilst the simple iodides are, for the most part, only very sparingly soluble. To this statement certain substituted ammonium iodides represent exceptions. Then, again, iodine itself only dissolves to a comparatively small extent in nitrobenzene; the saturated solution at 18° contains approximately 0·2 mol. per litre. The very slight miscibility of nitrobenzene and water represents another factor of importance in connexion with the investigation of the soluble polyiodides, for this permits of a direct comparison of two different solutions of polyiodides which are in equilibrium with one another.

In the experiments described in this paper, an attempt has been made to ascertain the several types of polyiodides which are formed in nitrobenzene solutions and the relationships which exist between the various types by a study of the distribution of iodine and iodides between nitrobenzene and water. The polyiodides of potassium have been examined more particularly, but comparative measurements have also been made in which the polyiodides of ammonium, substituted ammonium and the other alkali metals were submitted to investigation.

Jakowkin (*Zeitsch. physikal. Chem.*, 1894, **13**, 539; 1896, **20**, 19) has shown that the proportions of free and combined iodine in dilute aqueous solutions containing iodine and alkali or alkaline earth metal iodides are in agreement with the assumption of a dissociation equilibrium corresponding with the equation $MI_3 \rightleftharpoons MI + I_2$. If v is the volume of solution which contains one mol. of iodine as titrated by sodium thiosulphate solution, a the number of mols. of iodide contained in this volume, x the fraction of the iodine which is present in the free state, then the concentrations of the tri-iodide, iodide, and iodine are repectively $(1-x)/v$, $(a-1+x)/v$, and x/v, and the equilibrium constant K is given by the equation:

$$K=\frac{x(a-1+x)}{v(1-x)} \quad (1).$$

When the value of the constant K is known, and v and a for a given solution are determined by experiment, this equation may be used to calculate x/v, the concentration of the free iodine in the solution.

The possibility of obtaining the concentration of the free iodine in an aqueous iodine-iodide solution by this means has been utilised in the examination of nitrobenzene solutions of the polyiodides. When, for example, potassium iodide and iodine are shaken at constant temperature with excess of nitrobenzene and water until a condition of equilibrium is reached, two solutions containing polyiodides are obtained. The distribution of the iodine and potassium iodide between the two liquids is determined by definite partition coefficients characteristic of these substances, and by the formation of more or less stable polyiodides.

According to Jakowkin's investigations (*loc. cit.*), the nature of aqueous iodide-iodine solutions is very simple; provided the concentrations of the iodide and iodine do not exceed certain limits, the equilibrium can be represented by the equation $KI_3 \rightleftharpoons KI + I_2$. The concentration of the free iodine in any such solution can be determined from equation (1), and if the ratio of distribution of iodine between nitrobenzene and water is known, the concentration of the free iodine in the nitrobenzene solution, which is in equilibrium with this aqueous solution, may be deduced.

According to this method, the uncombined iodine in nitrobenzene solutions containing iodine and potassium iodide in different proportions has been estimated. For the application of the method, measurements of the constant *K* at 18° and of the partition of iodine between nitrobenzene and water at different concentrations were required.

The constant *K* was determined by the method previously described (Dawson, Trans., 1901, **79**, 238). Carbon tetrachloride was used in measuring the concentration of the free iodine in the aqueous solutions. The two following experiments give the value of the partition-coefficient of iodine between carbon tetrachloride and water at 18° ± 0·02°. The concentrations are expressed in mols. per litre.

TABLE I.

Iodine concentration in CCl_4.	Iodine concentration in H_2O.	Distribution ratio.
0·03438	0·0004158	82·7
0·04426	0·000535	82·8
	Mean	82·8

This value of the ratio was used in obtaining the free iodine concentration of the two aqueous iodide-iodine solutions examined, for which the experimental data and the calculated values of *K* are contained in table II.

TABLE II.

Aqueous solution.	Carbon tetrachloride solution.	*K*.
0·1 molar KI 0·02413 ,, iodine	0·02975 molar iodine	0·001153
0·1 ,, KI 0·02479 ,, iodine	0·03083 ,, ,,	0·001153

To ascertain the ratio of distribution of iodine between water and nitrobenzene, experiments at widely different concentrations were made. The quantities of the two liquids employed were largely increased as the iodine concentration was diminished, and in the case of the most dilute solutions 100 c.c. of nitrobenzene and 750 c.c. of water were used, the iodine concentration in the aqueous layer being obtained by titration of 500 c.c. with *N*/100 thiosulphate solution. The experimental data are contained in table III, the concentrations being expressed in mols. per litre.

TABLE III.

Iodine concentration in $C_6H_5{\cdot}NO_2$.	Iodine concentration in H_2O.	Distribution ratio.
0·03325	0·000191	174
0·03610	0·000207	174
0·0780	0·000451	173
0·0854	0·0004965	172
0·2275	0·001330	171
0·3328	0·001893	176

The numbers in the third column indicate that the ratio of distribution of iodine between the two solvents is independent of the concentration, and the mean value is taken as 174. From this constancy, the conclusion may be drawn that the molecular complexity of iodine in the two solvents is the same.

Two experiments were also made to ascertain the ratio of distribution of potassium iodide between the two solvents. In consequence of the slight miscibility of the two liquids, this ratio differs in all probability very considerably from the ratio of the solubilities of the iodide in water and dry nitrobenzene. Both determinations were made on saturated solutions, a large volume of nitrobenzene and a small volume of water being shaken up with excess of potassium iodide; after remaining in the thermostat for about twenty-four hours, the concentration of the solutions was determined, the nitrobenzene solution being extracted for this purpose with successive small quantities of water, which was then evaporated to dryness. Table IV gives the experimental data, the concentrations being expressed in mols. per litre.

TABLE IV.

KI in water.	KI in nitrobenzene.	Distribution ratio.
6·05	0·00114	5300
6·05	0·00108	5600
	Mean	5450

The results obtained in these preliminary experiments have been utilised in the estimation of the free iodine in nitrobenzene solutions containing known quantities of potassium iodide and iodine. In order to illustrate the essential features of the experimental method, the mode of procedure which was tried in the first instance may be described. A definite quantity of water was shaken at 18° with successive quantities of a nitrobenzene solution (referred to as solution *A*) until the composition of the aqueous solution had become constant, and no change could be observed when it was agitated with a further quantity of solution *A*. The concentration of the iodine in the aqueous solution was then determined by titration, and that of the iodide by evaporation of a measured volume. By means of equation (1), the concentration of the free iodine in the aqueous solution is then obtained, and by multiplication of this value by the partition-coefficient of iodine distributing itself between nitrobenzene and water, the concentration of the free iodine in solution *A* is deduced.

Two or three preliminary experiments sufficed to show that this method of reaching the aqueous solution in equilibrium with solution *A* by a process of approximation could not be conveniently applied as a general method because of the large quantities of solution *A* required.

An alternative method, which consisted in shaking up solution *A* with aqueous potassium iodide solutions, the original concentrations of which were respectively greater and less than the concentration of the equilibrium solution, was found to be more convenient. The composition of the two aqueous solutions, after shaking with *A*, was determined, and from the changes in composition the composition of the equilibrium aqueous solution was deduced by interpolation. For an accurate measurement of the desired concentration by this method, the two aqueous solutions which are shaken up with solution *A* must not differ too greatly from the equilibrium solution the composition of which is sought. On account of the relatively small quantities of iodine which are removed when the solution *A* is shaken with the aqueous solutions, the addition of iodine to these solutions was not considered necessary; the iodine concentration of the equilibrium solution has therefore been simply determined by interpolation from the iodine concentrations of the two aqueous solutions used in the estimation of the equilibrium concentration of the iodide.

The actual data obtained in the determination of the aqueous solution which is in equilibrium with a nitrobenzene solution containing potassium iodide and iodine in quantities corresponding with the formula 0·1 molar (KI + 7I) may be recorded as an illustration of the application of the method. Twenty-five c.c. of this solution were shaken with 50 c.c. of (1) 0·010 molar aqueous potassium iodide, (2) 0·015 molar aqueous potassium iodide. After shaking, the first aqueous solution was found to contain 0·0112 mol. of potassium iodide and 0·00334 mol. of iodine per litre, and the second solution 0·0140 mol. of potassium iodide and 0·00369 mol. of iodine per litre. The two original solutions are thus seen to contain respectively less and more potassium iodide than the equilibrium solution, and by interpolation this is found to contain 0·0125 mol. of potassium iodide per litre; the interpolated iodine concentration corresponding with this is 0·00351 mol. per litre.

In this way the composition of the aqueous solutions in equilibrium with 0·1 molar nitrobenzene solutions of potassium iodide, containing respectively 2, 3, 4, 5, 6, 7 and 8 atoms of iodine per mol. of iodide, has been determined. The data are collected in table V, concentrations being expressed in mols. per litre.

TABLE V.

	Composition of nitrobenzene solution.	Composition of aqueous solution.	
		Potassium iodide.	Iodine.
(1)	0·1 molar (KI + 2I)	6·05	0·00050
(2)	,, (KI + 3I)	0·62	0·00435
(3)	,, (KI + 4I)	0·22	0·00535
(4)	,, (KI + 5I)	0·046	0·00480
(5)	,, (KI + 6I)	0·022	0·00412
(6)	,, (KI + 7I)	0·0125	0·00351
(7)	,, (KI + 8I)	0·0073	0·00305
(8)	,, KI saturated with iodine	0·0027	0·00226

In the first and last experiments the two solutions were in contact with undissolved potassium iodide and iodine respectively. On examination of the two series of numbers it is seen that the concentration of the iodide in the aqueous solution decreases rapidly as the relative proportion of iodine in the nitrobenzene solutions increases; the ratio of the iodide concentrations for the first and last solutions is approximately 2200 : 1. The iodine concentrations of the aqueous solutions are all very small compared with those of the corresponding nitrobenzene solutions; for the first solution, the ratio of these iodine concentrations is 1 : 200, although the concentration of the iodide in the aqueous solution is sixty times as large as it is in the nitrobenzene solution. These relationships indicate that nitrobenzene is a solvent which is most markedly favourable to the existence of the polyiodides which are the subject of this investigation.

A much clearer insight into the nature of the relationships, which exist between the corresponding aqueous and nitrobenzene solutions, is obtained when the concentrations of the free iodine are calculated in the manner already described. In table VI the first column gives the composition of the nitrobenzene solution; the second, the volume (v) in litres of the aqueous solution which contains 1 mol. of iodine titrated by thiosulphate solution; the third, the molar ratio (a) of iodide to iodine in the aqueous solution; the fourth, the fraction (x) of the total iodine present in the free state; the fifth, the concentration (x/v) of the free iodine in the aqueous solution; and the sixth, the concentration ($174x/v$) of free iodine in the nitrobenzene solution.

TABLE VI.

Composition of nitrobenzene solution.	v.	a.	x.	x/v.	$174\,x/v$.
0·1 molar (KI + 2I)	2000	12100	0·00019	0·000000095	0·0000165
,, (KI + 3I)	230	142	0·00189	0·0000082	0·00143
,, (KI + 4I)	187	41·1	0·00539	0·0000288	0·00504
,, (KI + 5I)	208	9·58	0·0270	0·000130	0·0226
,, (KI + 6I)	243	5·31	0·060	0·000247	0·0430
,, (KI + 7I)	285	3·56	0·110	0·000386	0·067
,, (KI + 8I)	328	2·40	0·193	0·00059	0·103
,, KI saturated with iodine	442	1·20	0·44	0·00100	0·174

The numbers in the last column are those to which attention must be directed. These have been calculated on the assumption that equation (1) expresses the relationship between free and combined iodine in the aqueous solutions which are in equilibrium with the various nitrobenzene solutions. With the exception of the first aqueous solution, all these are within the limits for which the validity of equation (1) may be said to have been established experimentally (compare Jakowkin, *loc. cit.*). For the solution saturated with iodine, the experiments of Noyes and Seidensticker (*Zeitsch. physikal. Chem.*, 1898, **27**, 357) indicate that the quantities of free and combined iodine are in agreement with the requirements of the dissociation equation $KI_3 \rightleftharpoons KI + I_2$. It is therefore only in respect of the first solution, where the molar ratio of iodide to iodine reaches the very high value of 12100, that the validity of this equation may be said to lack experimental proof. That any polyiodide other than potassium tri-iodide is present in the saturated potassium iodide solution is, however, very improbable, and it may be confidently assumed that the concentration of the free iodine in this solution may also be obtained at least approximately by means of equation (1). In consequence of the high concentration of the iodide in the aqueous solution, the distribution of the free iodine between the two liquids will no doubt in this case undergo an alteration which is considerably greater than that resulting from the "salting-out" action in the case of the other solutions, and to this extent the calculated concentration of free iodine in the first nitrobenzene solution is somewhat doubtful.

Comparing the numbers in the last column of the preceding table, it is evident that the free iodine concentration increases enormously as the molar ratio of iodine to iodide increases from one to four; the ratio of the values for the solutions KI_9 and KI_3 is 6200 : 1. In the interpretation of these numbers it may be recalled that the existence of the polyiodides KI_3 and KI_9 has been established as the result of solubility measurements, and that these represent the lowest and highest polyiodides which are capable of existence in nitrobenzene solutions. As yet, however, no evidence of the existence of definite intermediate types has been brought forward. From the fact that all the polyhalogen compounds of the alkali metals which have been prepared as crystalline substances are of the types MX_3 or MX_5 (compare Wells, *Zeitsch. anorg. Chem.*, 1892, **1**, 85; Wells and Wheeler, *ibid.*, 1892, **1**, 442; 1892, **2**, 255), that the polyiodides of the alkali metals, the existence of which, in the free state, is indicated by the iodine tension measurements of Abegg and Hamburger (*Zeitsch. anorg. Chem.*, 1906, **50**, 403), are of the types MI_3, MI_5, MI_7, or MI_9, and that the crystallised polyiodides of the substituted ammonium bases are of these same types, it might be expected that the intermediate polyiodides KI_5 and KI_7 are contained in nitrobenzene solutions the composition of which corresponds with these formulæ. On the other hand, it is possible that such solutions represent mixtures of the highest and lowest polyiodides in accordance with the equations (*a*) $3KI_5 = 2KI_3 + KI_9$, and (*b*) $3KI_7 = KI_3 + 2KI_9$.

It appears possible to decide which of the two views corresponds with fact by the following consideration. If the 0·1 molar solution of the composition (KI + 4I) represents a mixture of the tri- and ennea-iodide in accordance with equation (*a*), the concentration of the ennea-iodide in the solution should be 0·033 molar. Measurement of the free iodine concentration in a 0·033 molar KI_9 solution gave 0·0405 mol. per litre, while according to the previous table a 0·1 molar solution of the composition (KI + 4I) contains 0·00504 mol. free iodine per litre. These numbers are as 8 to 1, and the very large difference between the free iodine concentrations of these two solutions must be interpreted as in favour of the view that a nitrobenzene solution of the composition (KI + 4I) contains a definite polyiodide KI_5 as the chief component. By similar reasoning it is possible to show that the polyiodide KI_7 is present in nitrobenzene solutions which contain more iodine.

The conclusion that four polyiodides, KI_3, KI_5, KI_7 and KI_9, are formed in nitrobenzene solution agrees very satisfactorily with the numbers which express the free iodine concentrations of the nitrobenzene solutions (1) to (8) in table VI if we assume that chemical dissociation of the polyiodides takes place in accordance with the scheme: $KI_9 \rightleftarrows KI_7 + I_2$; $KI_7 \rightleftarrows KI_5 + I_2$; $KI_5 \rightleftarrows KI_3 + I_2$; $KI_3 \rightleftarrows KI + I_2$. Although it is not possible to subject the four stages in the dissociation process to a separate minute analysis, a comparison of the percentage amounts of free iodine in 0·1 molar solutions of the composition KI_3, KI_5, KI_7 and KI_9 respectively gives some idea of the extent of the dissociation in the several stages. The numbers in table VII represent the percentage amounts of free iodine in terms of the total iodine as titrated by thiosulphate solution.

Table VII.

Composition of solution.	KI_3.	KI_5.	KI_7.	KI_9.	Saturated with iodine.
Percentage iodine dissociation	0·016	2·5	14	26	32

From these numbers it is evident that the dissociation of the tri-iodide is extremely small, whereas that of the ennea-iodide is very considerable; the value 26 can only be interpreted on the assumption that dissociation in the ennea-iodide solution has taken place, not only in accordance with the first equation, but also to an appreciable extent according to the second. In reference to the solution saturated with iodine, it may be noted that this contains 5·50 mols. of iodine per mol. of iodide. Of this, 32 and 68 per cent. respectively are present in the free and combined states; the ratio of combined iodine to iodide is therefore expressed by the formula $KI_{8\cdot3}$, from which it is evident that the dissociation of the ennea-iodide is very considerably diminished in presence of the excess of iodine corresponding with the saturated solution.

Influence of the Concentration of the Solution on the Dissociation of KI_9.—With the object of obtaining further information in regard to the dissociation of the polyiodides, the amount of free iodine in ennea-iodide solutions of different concentrations has been examined. In these experiments, 0·01, 0·033, 0·1 and 0·48 molar solutions of the composition KI_9 were shaken at 18° with aqueous iodide solutions of known concentration, and from the changes undergone by the aqueous solutions the composition of the aqueous solution which is in equilibrium with each of the four nitrobenzene solutions was deduced. The concentration of the free iodine in these was then calculated as previously described. Table VIII contains the results of this investigation, the several columns of figures having the signification given previously in connexion with table VI.

Table VIII.

Concentration of KI_9 solution.	v.	a.	x.	x/v.	174 x/v.	Dissociation per cent.
0·48 molar	105·3	2·00	0·100	0·000950	0·165	8·6
0·10 ,,	328	2·40	0·193	0·000590	0·103	26
0·033 ,,	617	5·06	0·144	0·000233	0·0405	30
0·01 ,,	1600	12·8	0·134	0·0000838	0·0146	36

The iodine dissociation evidently increases with the dilution of the solution, and the observed variation leads to the conclusion that in more concentrated solutions, such as were examined by means of solubility measurements, the ennea-iodide is dissociated to a comparatively small extent. The calculated value of the dissociation is based on the assumption that the iodine distribution is determined in all cases by the ratio 174; the uncertainty hereby involved increases with the concentration, and on this account more concentrated solutions were not submitted to examination.

Dissociation of different Ennea-iodides.—The experiments of which an account has so far been given refer solely to potassium iodide solutions. If polyiodide solutions of the other alkali metals were subjected to a minute examination, similar relationships would no doubt be found. To ascertain whether quantitative differences in the degree of chemical dissociation are exhibited, solutions containing lithium, sodium, potassium, rubidium, cæsium, ammonium and tetramethylammonium iodide have been compared. To effect this comparison in a complete manner would have involved the determination of the composition of the aqueous solutions which are in equilibrium with the tri-, penta-, hepta-, and ennea-iodide solutions of each of the alkali metals and ammonium bases. The fact that the accurate measurement of the free iodine in the tri-iodide solutions necessitates the use of large quantities of materials, and that the validity of equation (1) for the concentrated aqueous solutions has not been experimentally demonstrated, has limited the inquiry in the case of the tri-iodides to sodium and potassium. For the rest, it was considered sufficient to compare the ennea-iodide solutions, and this comparison has been made for 0·1 molar solutions without determining exactly the composition of the aqueous solutions with which the nitrobenzene solutions are in equilibrium.

In this comparative investigation, 50 c.c. of each of the ennea-iodide solutions were shaken with an equal volume of water, and the concentration of iodide and iodine in the aqueous solution determined.

In table IX, the iodide under investigation is indicated in the first column, the second and third columns give the concentration of the iodide and iodine in the aqueous solutions, the fourth gives the calculated concentration of free iodine in the nitrobenzene solutions, and the fifth the percentage iodine dissociation.

TABLE IX.

	Aqueous solution.		Nitrobenzene solution.	
Iodide.	Iodide.	Iodine.	Free iodine.	Dissociation per cent.
$N(CH_3)_4I_9$	0·00015	0·00075	0·104	26
CsI_9	0·00117	0·00105	0·110	27
RbI_9	0·00387	0·00189	0·102	25
KI_9	0·00665	0·00281	0·101	25
NH_4I_9	0·0120	0·00471	0·104	26
NaI_9	0·0308	0·0135	—	—
LiI_9	0·0456	0·0225	—	—

In this table the iodides are arranged in the order of increasing concentration of the aqueous solution. From the numbers in the second and third columns, it is evident that the quantities of the iodides and of iodine which are removed by water from the several ennea-iodide solutions vary very considerably; the particular iodide in a given ennea-iodide solution can indeed be at once recognised by the intensity of the colour of the aqueous extract. In consequence of the removal of iodide by the water, the composition of the nitrobenzene solution changes to an extent which depends on the particular iodide present. This change is negligible in the case of tetramethylammonium, small for cæsium and rubidium, considerable for potassium and ammonium, and very large for sodium and lithium. Although in consequence of this circumstance the data obtained for the various solutions are not all comparable, it appears at first sight as if the dissociation depends very largely on the metal (or radicle) contained in the ennea-iodide solution. If, however, the concentration of the free iodine in the various nitrobenzene solutions is calculated from the composition of the corresponding aqueous solutions, a very nearly constant value is obtained, as is evident from the numbers in the fourth and fifth columns of the table. That the values of the free iodine concentration and the dissociation calculated in this way are approximately the same as those which would be obtained from the aqueous solutions in equilibrium with the accurately 0·1 molar ennea-iodide solutions is shown by the close agreement of the values in the case of potassium; these are respectively 25 and 26 per cent. for the iodine dissociation.

It should be noted that the aqueous solution obtained by extraction of the tetramethylammonium ennea-iodide solution with water contains more iodine than iodide, and in the calculation it has been assumed that all the iodide is present in the form of tri-iodide. The same constant, $K=0{\cdot}001155$, has been used as determining the equilibrium in the aqueous solution for all the iodides examined. Jakowkin's experiments (*loc. cit.*) indicate that this is justified for sodium and lithium solutions, and a determination for a cæsium iodide solution gave the same value for the constant as has been found in the case of potassium iodide.

On account of the large quantities of iodide and iodine which are extracted when the ennea-iodide solutions of sodium and lithium are shaken up with an equal volume of water, the data for these solutions in table IX cannot be utilised for the calculation which has been made in the case of the other five solutions. For the sodium ennea-iodide solution, the composition of the aqueous solution in equilibrium with it has, however, been determined by the method previously described; this solution was found to contain 0·080 mol. sodium iodide and 0·0248 mol. iodine per litre, and the proportion of free iodine in the ennea-iodide solution which is calculated from these numbers is 22 per cent., which agrees fairly well with the dissociation found in the case of the other iodides.

The above comparative measurements lead to the conclusion that the ennea-iodides of the alkali metals and ammonium bases are chemically dissociated to the same extent. It is evident that this may be explained if we assume that the free iodine is a dissociation product of iodine ions in accordance with the scheme: $I_9' \rightleftharpoons I_7' + I_2$; $I_7' \rightleftharpoons I_5' + I_2$; $I_5' \rightleftharpoons I_3' + I_2$; $I_3' \rightleftharpoons I' + I_2$. In support of this view, measurements of various physical properties of the polyiodide solutions will be communicated in a further paper.

As previously mentioned, a comparison of the quantities of iodine in the aqueous solutions obtained by shaking together a 0·1 molar nitrobenzene solution of iodine with water and excess of potassium or sodium iodide has been made. In the case of potassium, the aqueous solution was found to contain 6·05 mols. of iodide and 0·00050 mol. of iodine per litre, while the sodium solution contained 8·11 mols. of iodide and 0·0011 mol. of iodine per litre. The free iodine in the two nitrobenzene solutions corresponding with these data is about 0·02 per cent.; the chemical dissociation of both the tri-iodides is therefore very small. The very unequal distribution of the iodine in these circumstances, coupled with the fact that the tri-iodides are so readily soluble in water, leads to the supposition that the tri-iodides in the nitrobenzene solution are combined in some way with the solvent. The fact that water removes widely different quantities of iodides and iodine from ennea-iodide solutions of the various alkali metals and ammonium bases can also be accounted for on this hypothesis if the compounds formed by the polyiodides with the nitrobenzene are of different degrees of stability.

The author is indebted to the Research Grants Committee of the Royal Society for a grant, which has partly defrayed the cost of the materials used in this investigation. To Mr. C. G. Jackson his thanks are due for assistance in some of the measurements recorded in the paper.

PHYSICAL CHEMISTRY LABORATORY,
THE UNIVERSITY,
LEEDS.

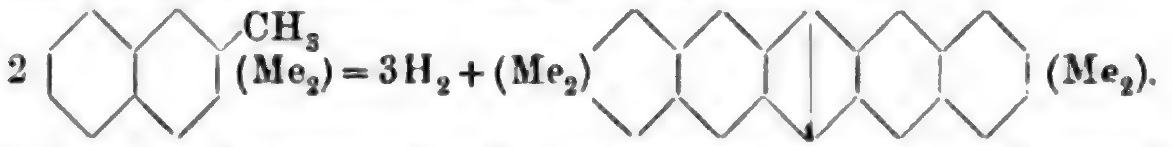
CXXVI.—*The Study of the Absorption Spectra of the Hydrocarbons isolated from the Products of the Action of Aluminium Chloride on Naphthalene.*

By ANNIE HOMER, Fellow of Newnham College, and
JOHN EDWARD PURVIS, M.A.

FROM the products of the action of aluminium chloride on naphthalene, besides *ββ*-dinaphthyl previously isolated by Friedel and Crafts from the same reaction, there have been isolated three new hydrocarbons which have been described in detail by one of us (Homer, Trans., 1907, **91**, 1103). The substances isolated were:

(i) $C_{14}H_{16}$, a homologue of naphthalene, either tetramethyl- or diethyl-naphthalene, more probably the former; (ii) $C_{20}H_{14}$, ββ-dinaphthyl; (iii) $C_{26}H_{22}$, a substance supposed to be a homologue of dinaphthanthracene, $C_{22}H_{14}$; and (iv) $C_{40}H_{26}$, probably tetranaphthyl.

ββ-Dinaphthyl is formed by the condensation of two naphthalene molecules. It was thought that the hydrocarbon $C_{40}H_{26}$ was formed by the condensation of either two ββ-dinaphthyl or four naphthalene molecules, more probably by the former, as an increase in the time allowed for the action of aluminium chloride on naphthalene, or a rise in the temperature at which the reaction was conducted, caused a decrease in the amount of the hydrocarbon $C_{20}H_{14}$ and an increase in the amount of the hydrocarbon $C_{40}H_{26}$ produced. It was suggested that the substance $C_{26}H_{22}$ was a homologue of dinaphthanthracene, $C_{22}H_{14}$, and its formation from alkylnaphthalenes, which are also formed during the reaction, was given as follows:



The intense fluorescence of the substance suggested the presence of an anthracenoid linking.

In the method of formation thus proposed, hydrogen would be eliminated from a β-methyl group of trimethylnaphthalene. It was thought (*loc. cit.*) that further evidence as to the constitution of the respective products of the reaction in question might be produced from a comparative study of their absorption spectra with that of naphthalene; and it was also suggested that the absorption spectrum of the hydrocarbon $C_{26}H_{22}$ should be compared with that of the supposed parent substance, dinaphthanthracene, $C_{22}H_{14}$, and of picene, the isomeride of dinaphthanthracene.

It was with these objects in view that the investigation here described was undertaken.

Experimental.

The hydrocarbons $C_{14}H_{16}$, $C_{20}H_{14}$, $C_{40}H_{26}$, $C_{26}H_{22}$, were prepared according to the methods given in the paper by Homer (*loc. cit.*).

The standard strength of our solutions was taken as *N*/1000, a normal solution being considered as a solution containing one gram-molecular weight of solute in 1000 c.c. of the solution.

The adjustable cell used has been previously used and described by Purvis and Foster (*Proc. Camb. Phil. Soc.*, 1907, **14**, 381). It is a modification of the very useful instrument described by Baly and Desch (Trans., 1904, **85**, 1029).

The results of the study of the absorption spectra of the substances under consideration have been plotted in the accompanying curves so that the abscissæ represent oscillation frequencies, and the ordinates the logarithms of relative thicknesses of the solution. From eye observations we could observe directly the bands due to the hydrocarbon $C_{26}H_{22}$, and the absence of bands in the hydrocarbons $C_{40}H_{26}$, $C_{20}H_{14}$, $C_{14}H_{16}$; but in order to compare the absorption curves with those of other substances like naphthalene we decided to plot the curves in exactly the same way, so as to obtain comparable results.

I. *Naphthalene and* $C_{14}H_{16}$.

The absorption spectrum of naphthalene has been given in detail by Hartley (Trans., 1881, **39**, 153), who has shown that there are four bands characteristic of this substance. Their mean wave-lengths are:

2855 2726 2631 2550

which correspond with oscillation frequencies of:

3451 3690 3840 3921

The curve for an *N*/1000 solution of the hydrocarbon $C_{14}H_{16}$ in alcohol also shows four bands (Fig. 1). The mean oscillation frequencies of these bands are as follow:

3434 3562 3680 3776

These four bands are thus nearer the red end of the spectrum and appear to be less persistent than the corresponding bands in the naphthalene curve. The curve for the hydrocarbon $C_{14}H_{16}$ is therefore in accordance with the suggestion in the previous paper that this substance is an alkyl derivative of naphthalene. It is suggested on p. 1327 that the methyl groups are probably in the 1, 4, 5, 8 positions.

II. *The Hydrocarbons* $C_{20}H_{14}$ *and* $C_{40}H_{26}$.

N/10,000 solutions of these compounds in benzene were compared. It was found that stronger solutions did not show selective absorption. The curves for both these substances in benzene show only two weak bands (Fig. 2). The mean oscillation frequencies of these bands were:

For $C_{20}H_{14}$	3184	3430
For $C_{40}H_{26}$	3060	3200

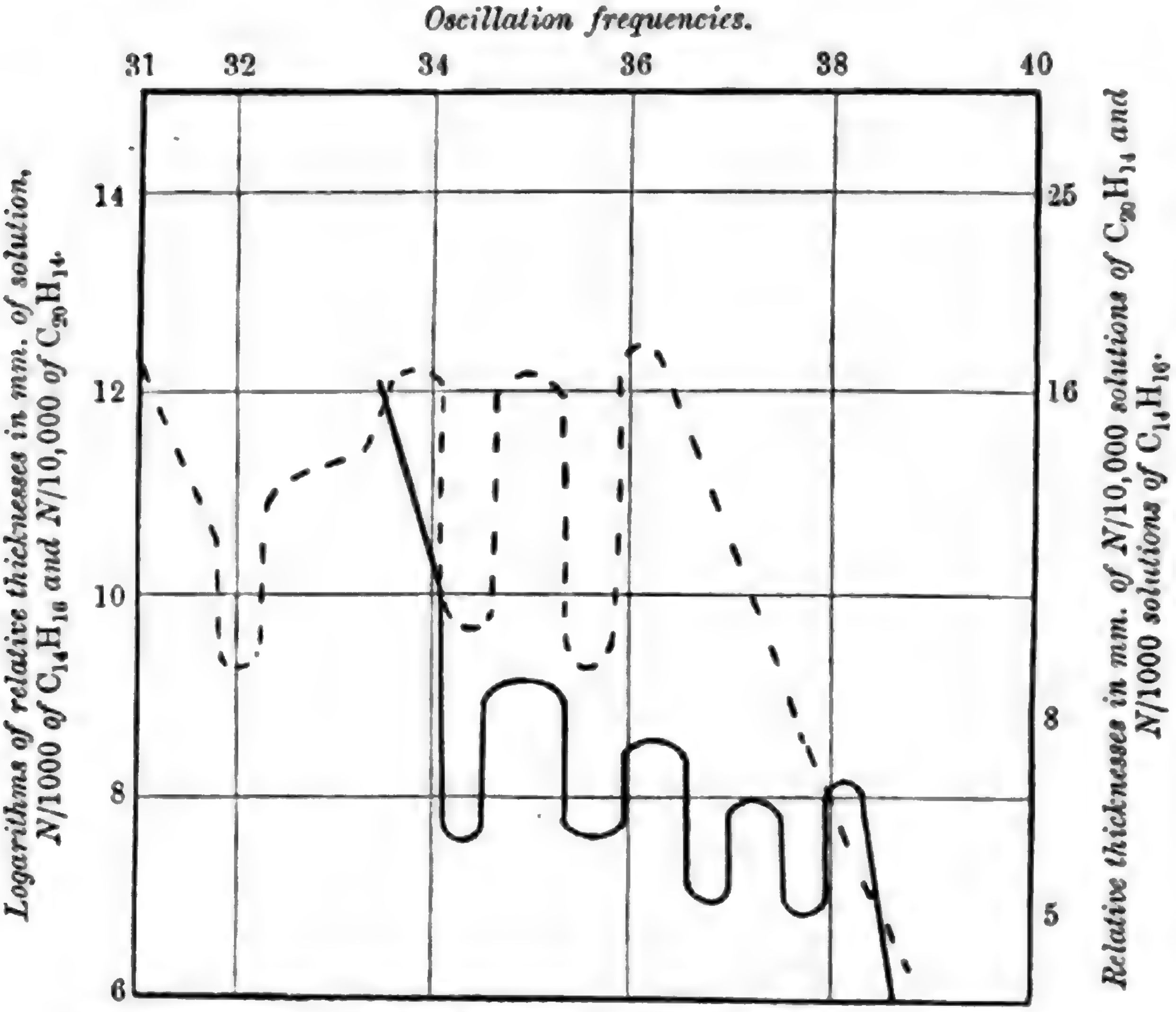
The bands exhibited by the solutions of the hydrocarbon $C_{40}H_{26}$ are nearer the red end of the spectrum than those exhibited by solutions of the hydrocarbon $C_{20}H_{14}$; but in the former case they are so weak that they may be regarded as traces.

Since benzene solutions of the hydrocarbons $C_{20}H_{14}$ and $C_{40}H_{26}$ exhibit the same type of curve, it seems reasonable to infer that these substances have a similar constitution. The hydrocarbon $C_{20}H_{14}$ has been shown to be $\beta\beta$-dinaphthyl by Watson Smith (Trans., 1877, **15**, 551; 1879, **17**, 224) and Chattaway (Trans., 1895, **67**, 653).

The hydrocarbon $C_{40}H_{26}$ therefore probably has the constitution which has already been suggested, namely, that of tetranaphthyl. At the present stage it is impossible to state how the two $\beta\beta$-dinaphthyl molecules have been condensed to yield tetranaphthyl.

In order to compare the absorption spectrum of $\beta\beta$-dinaphthyl with that of naphthalene, it was necessary to examine it in alcoholic solution. An $N/10,000$ solution of $\beta\beta$-dinaphthyl in alcohol (Fig. 1) shows three absorption bands of which the mean oscillation frequencies are:

FIG. 1.



Full curve —— $C_{14}H_{16}$ *in alcohol.* *N/1000 solution.*
Dash ,, - - - *ββ-Dinaphthyl* ($C_{20}H_{14}$) *in alcohol.* *N/10,000 solution.*

3204	3436	3556

It is remarkable that whilst naphthalene in alcoholic solution gives four bands, $\beta\beta$-dinaphthyl in the same solvent gives only three bands, although $\beta\beta$-dinaphthyl consists of two naphthyl groups.

Now there are two possible explanations of this phenomenon, which are as follows:

(i) *The diminished absorption power is due to steric hindrance.* The molecule of ββ-dinaphthyl may be so arranged in space that there is crowding within the molecule such that the vibrations of some of the carbon atoms within one naphthyl group are hindered by the too close proximity of vibrating atoms in the other naphthyl group. The effect of this hindrance will be evidenced by a decrease either in the rate or the amplitude of the vibrations of the atoms affected. In either case the effect of the steric hindrance will be evidenced by a diminished capacity for selectively absorbing light, although the increased size of the molecule will increase the general absorption.

(ii) *The diminished absorption power may be due to the twisting of one naphthyl group relatively to the other.* If there is twisting in one of the naphthyl groups, the atoms in that group will no longer vibrate in the same plane as the corresponding atoms in the other group. The twisting effect is probably more marked for some of the atoms than for the others. Consider the effect of this twisting in the two extreme cases, where :

(*a*) The atoms are practically not affected. In this case the effect of the vibrations of these atoms on a ray of light will be the same as that of the corresponding atoms in the other naphthyl group. That is to say, the corresponding atoms of the two naphthyl groups will augment each other's absorbing power.

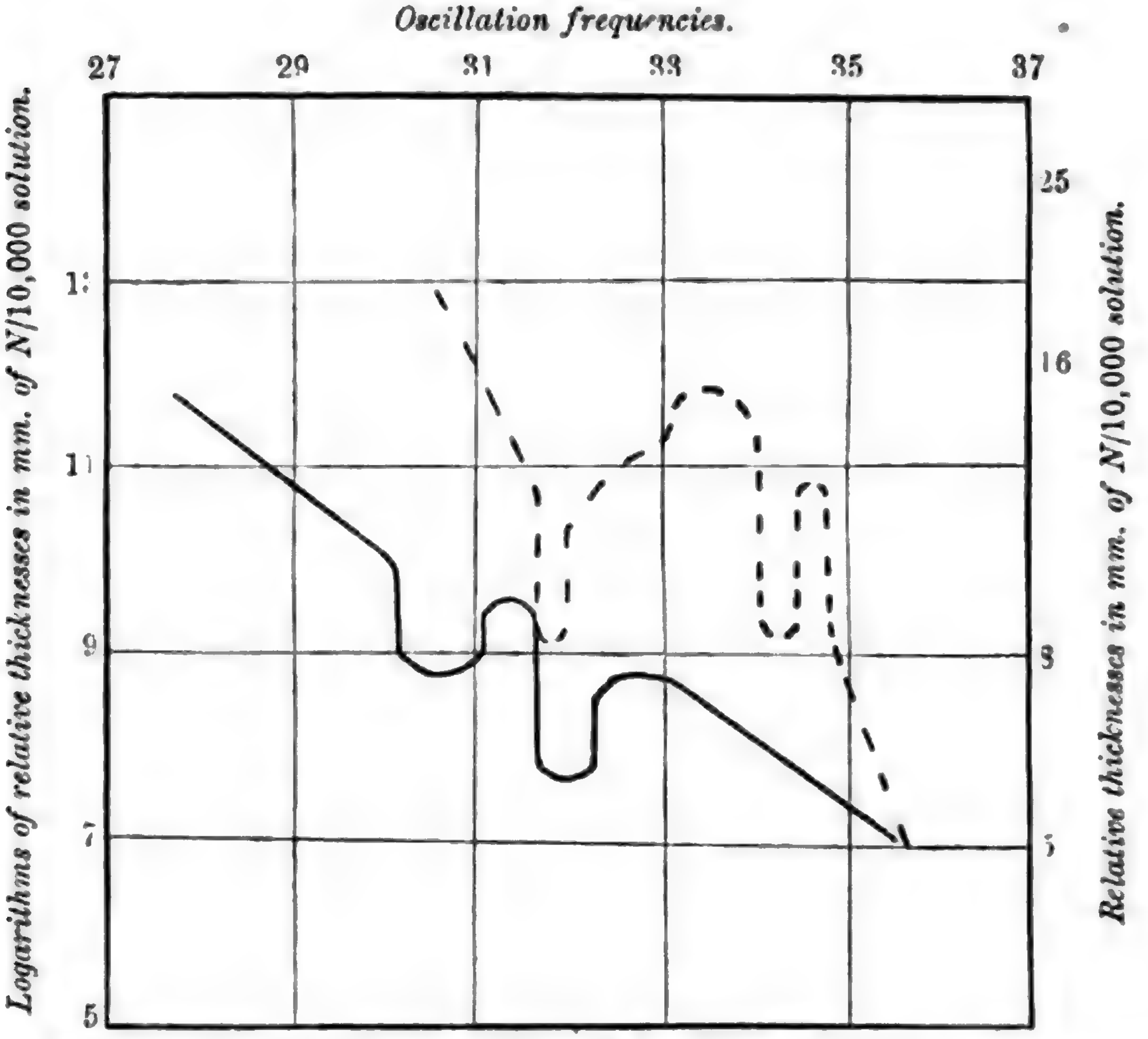
(*b*) The atoms are so much twisted that they vibrate in the same plane as the corresponding atoms in the other naphthyl group, but they are now in opposite phase. In this case the vibrating atoms nullify each other's effect on the ray of light. That is to say, if these atoms in the naphthalene molecule selectively absorbed light, they will now allow light to pass.

Moreover, between these two extremes cases there will be intermediate stages. But the total resultant effect of the various degrees of twisting of the second naphthyl group will be such that the selective absorption power of ββ-dinaphthyl is less than that of naphthalene.

If the above argument holds good, the decrease in selective absorption ought to be more marked in the case of tetranaphthyl. Owing to the insolubility of this hydrocarbon in alcohol it cannot be compared with naphthalene, but a glance at the curves in Fig. 2 shows that the two bands exhibited by this substance in benzene solution are so much weaker than the corresponding bands for ββ-dinaphthyl that they are practically eliminated. This fact is in accordance with the explanation offered above.

The effect of the increase in size of the molecule is shown by the fact that the alcoholic solution of ββ-dinaphthyl requires smaller concentration for complete absorption than that of naphthalene. At the same time there is a shift in the position of the bands towards the red end of the spectrum. The same effects are shown by benzene solutions of tetranaphthyl and ββ-dinaphthyl. In the case of ββ dinaphthyl, besides damping the third band, the benzene has slightly shifted the positions of the two remaining bands towards the red end of the spectrum.

FIG. 2.



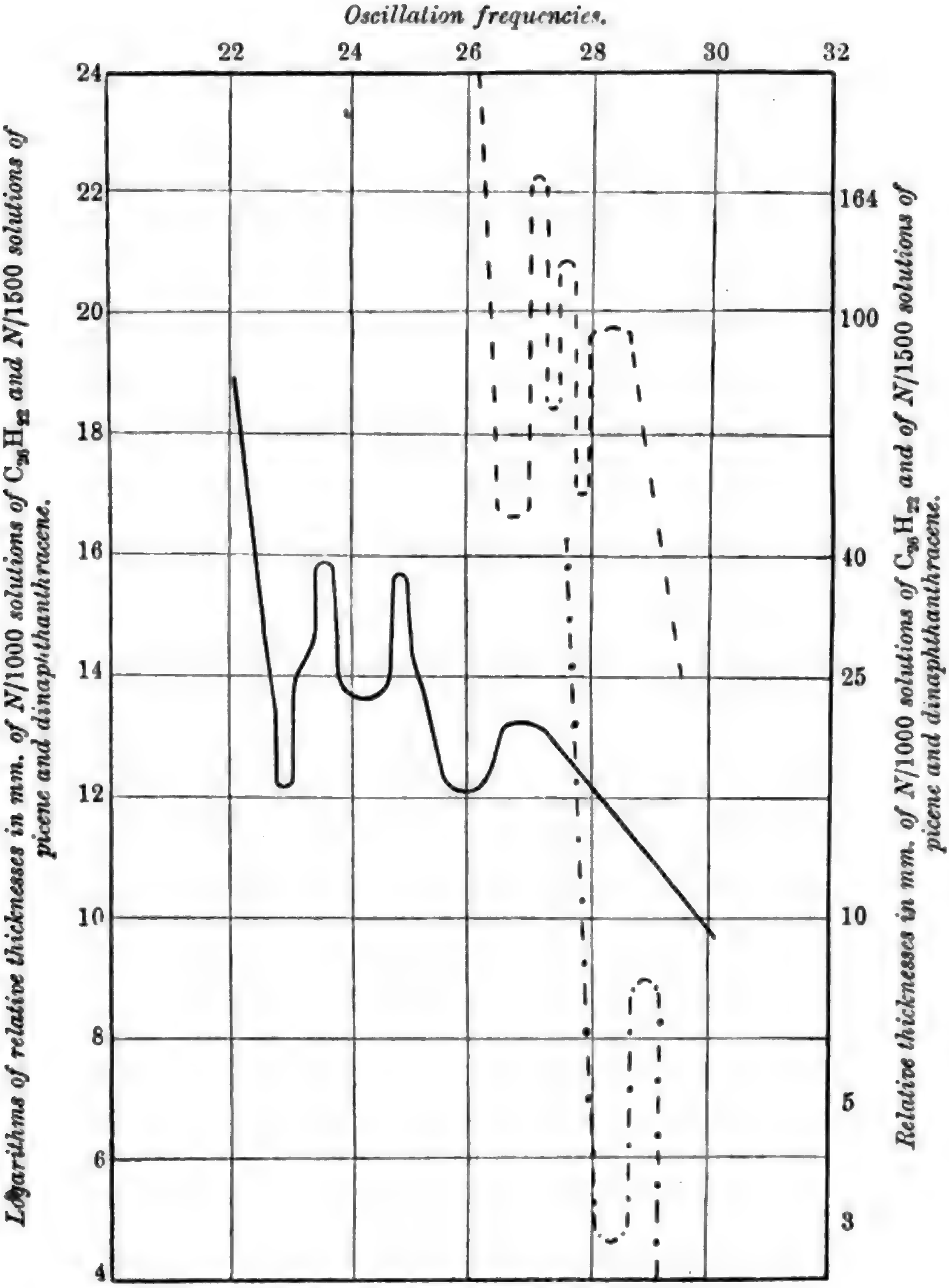
Full curve —— *Tetranaphthyl* ($C_{40}H_{26}$) *in benzene.* *N*/10.000 *solution.*
Dash ,, - - - *ββ-Dinaphthyl* ($C_{20}H_{14}$) *in benzene.* *N*/10,000 *solution.*

III. *Examination of Benzene Solutions of the Isomerides Picene and Dinaphthanthracene and of the Substance* $C_{26}H_{22}$.

The strongest solutions of picene and dinaphthanthracene which could be prepared were *N*/1500. In the case of the hydrocarbon $C_{26}H_{22}$ which is very soluble in benzene, it was found more convenient to use an *N*/1000 solution. The difference between the strengths of the solutions of the hydrocarbon $C_{26}H_{22}$ and of the isomerides did not affect the conclusions to be drawn from the resulting curves.

A comparative study of the curves shows that picene, as would be expected from Hartley's theory, exhibits a type of curve markedly

FIG. 3.



Full curve —— *N/1000 solution of $C_{26}H_{22}$ in benzene.*
Dash ,, - - - *N/1500 solution of picene in benzene.*
Dot and dash curve - · - *N/1500 solution of dinaphthanthracene in benzene.*

different from that of dinaphthanthracene (Fig. 3). The curve for *picene* (Fig. 3) shows three well-marked bands of which the mean oscillation frequencies are:

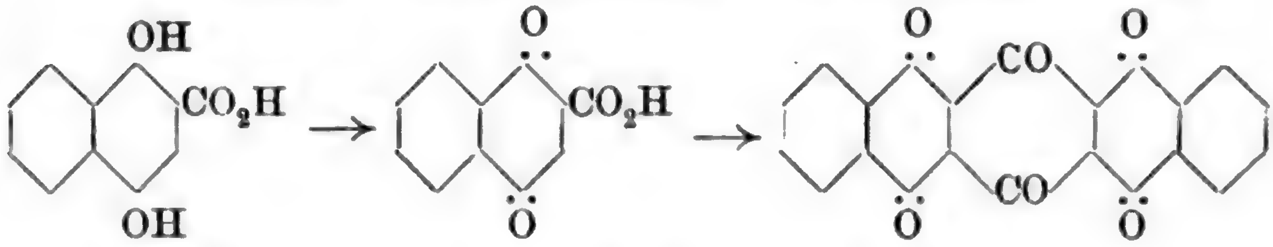
2670	2732	2784

The first of these bands is the most persistent. A solution of dinaphthanthracene of the same strength (Fig. 3) shows only one band, the mean oscillation frequency of which is 2840. The persistency of this band is not quite so marked as that of the first picene band. Besides the fact that picene has three bands, it is also remarkable that these bands are all much nearer the red end of the spectrum than the band of dinaphthanthracene. It seems therefore as though in picene the vibrations of the carbon atoms within the molecule have a greater amplitude than in the molecule of the isomeric dinaphthanthracene. Picene has been shown to have a phenanthrene structure by Bamberger and Chattaway (*Ber.*, 1893, **26**, 1751). Hartenstein (*Diss.*, Jena, 1892) has shown that dinaphthanthracene, from its method of formation, its properties, and the properties of its quinone, has a constitution similar to that of anthracene. Dinaphthanthracene was prepared by Hartenstein as follows:

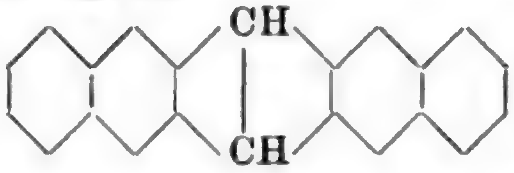
Disodium or dipotassium α-naphthaquinol was heated with carbon dioxide under pressure and from the products of the reaction, by suitable treatment, α-naphthaquinol-2-carboxylic acid was isolated. The acid thus obtained was treated with concentrated sulphuric acid at 70°, whereby two reactions took place:

(1) The acid was oxidised to α-naphthaquinonecarboxylic acid.

(2) The oxidation product condensed to form a substance $C_{22}H_8O_6$.



This condensation product by distillation with zinc dust was reduced to dinaphthanthracene, $C_{22}H_{14}$:



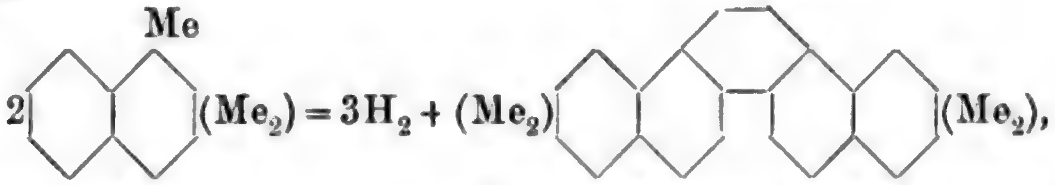
A small amount of dinaphthanthracene was also prepared by the same method by Russig (*J. pr. Chem.*, 1900, [ii], **62**, 30).

A study of the curve for the hydrocarbon, $C_{26}H_{22}$ (Fig. 3), shows that this substance has a constitution similar to that of picene and not of dinaphthanthracene, as had been previously supposed. The curve for *N*/1000 solutions of the hydrocarbon $C_{26}H_{22}$ in benzene shows three bands, of which the first is most persistent, with mean oscillation frequencies:

2290 2424 2584

The bands are much nearer the red end of the spectrum than those in the picene curve. These facts are in accordance with previous observations that the introduction of groups into the nucleus causes a shift in position towards the red end, but in this case the shift has been so great that the bands are in the visible portion of the spectrum.

The formation of the hydrocarbon $C_{26}H_{22}$ probably takes place as follows:



thus entailing the elimination of hydrogen from methyl groups in the α-position. Now from the facts known of the action of aluminium chloride on benzene and its homologues it seems justifiable to infer that in the corresponding reaction with naphthalene the monoalkylated naphthalene first formed would be converted into di-, tri-, and tetra-alkylated naphthalenes. Moreover, as there is no apparent reason against the supposition that symmetrical products would be formed, the obvious inference is that since in the trimethylnaphthalene, the forerunner of the hydrocarbon $C_{26}H_{22}$, there is one methyl group in the α-position, then the others are also in α-positions, and therefore in the hydrocarbon $C_{26}H_{22}$ the methyl groups are also in α-positions.

Applying the same method of reasoning with regard to the position of the methyl groups, the hydrocarbon $C_{14}H_{16}$ will probably be 1 : 4 : 5 : 8-tetramethylnaphthalene.

Summary.

The results of the comparative study of the absorption spectra of the substances under consideration indicate:

I. That the substance $C_{14}H_{16}$ is a naphthalene derivative, probably 1 : 4 : 5 : 8-tetramethylnaphthalene.

II. That the hydrocarbon $C_{40}H_{26}$ has a constitution similar to that of ββ-dinaphthyl, and is therefore probably tetranaphthyl.

III. That picene and dinaphthanthracene have markedly different absorption spectra.

IV. That the hydrocarbon $C_{26}H_{22}$ exhibits the same type of absorption curve as picene, and is therefore an alkyl derivative of picene.

There is still required some explanation of the intense fluorescence of the hydrocarbons $C_{40}H_{26}$ and $C_{26}H_{22}$. The investigation of these phenomena is a subject for future research.

The authors take this opportunity of thanking Prof. E. von Meyer for providing the sample of dinaphthanthracene from Dr. Hartenstein's specimen at Dresden, and also Prof. Bamberger and Dr. Chattaway for so kindly sending specimens of picene, without which the work embodied in this paper could not have been so satisfactorily concluded.

The authors also desire to express their thanks to the Research Fund Committee of the Chemical Society for a grant which has in part defrayed the expenses of this investigation.

The University Chemical Laboratory,
Cambridge.

CXXVII.—*Cholestenone.*

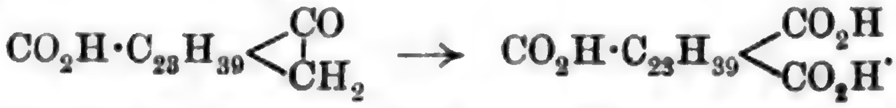
By Charles Dorée and John Addyman Gardner.

Cholesterol, which is an unsaturated secondary alcohol of the formula $C_{27}H_{46}O$, may be oxidised, under suitable conditions, to an unsaturated ketone, cholestenone, $C_{27}H_{44}O$ (Diels and Abderhalden, *Ber.*, 1904, **37**, 3092; Windaus, *Ber.*, 1906, **39**, 518). Although the CH·OH group of the cholesterol is converted to a carbonyl group in cholestenone, the behaviour of the two substances under the influence of reducing agents (*Ber.*, 1906, **39**, 884; 1908, **41**, 260) makes it doubtful whether their "carbon-skeleton" is identical in each case. In 1906 Windaus (*Ber.*, **39**, 2008) studied the oxidation of cholestenone, using neutral permanganate which, according to Tiemann and Semmler (*Ber.*, 1895, **28**, 1345), is less likely than other oxidising agents to produce intramolecular change. He obtained as the chief product a saturated keto-monocarboxylic acid, $C_{26}H_{42}O_3$, which contained one carbon atom less in the molecule than the parent substance, and which, on further oxidation, passed into a tricarboxylic acid, $C_{26}H_{42}O_6$.

These changes were, according to Windaus (*loc. cit.*), most simply explained by assuming that cholestenone contains a group, $CH\colon CH_2$, which is situated at the end of an open side-chain, so that the production of the acid may be represented by the following equation:

$$C_{25}H_{41}O\cdot CH\colon CH_2 + 5O = C_{25}H_{41}O\cdot CO_2H + H_2O + CO_2.$$

The tricarboxylic acid would then result by the rupture of the ring containing the carbonyl group thus:

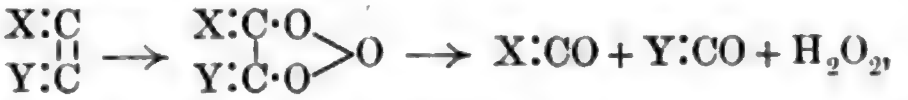


$$CO_2H\cdot C_{23}H_{39}<\begin{array}{l}CO\\ \,|\\ CH_2\end{array} \longrightarrow CO_2H\cdot C_{23}H_{39}<\begin{array}{l}CO_2H\\ CO_2H\end{array}.$$

The correctness of this explanation is based on the analyses of the ketonic acid and its derivatives, and their recognition as C_{26} compounds, a point which is somewhat difficult to settle by combustion alone; for example, Windaus found for the keto-carboxylic acid the figures C = 77·18, 77·75; H = 11·14, 11·18. These values agree equally well with the formula $C_{26}H_{42}O_3$, which requires C = 77·55, H = 10·52, and with $C_{25}H_{40}O_3$, which requires C = 77·26 and H = 10·38 per cent.

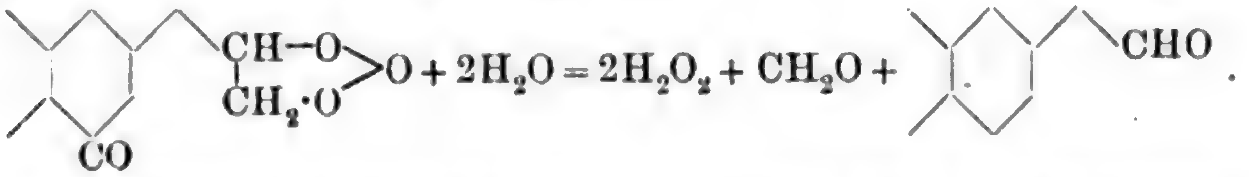
When the analyses of all the derivatives prepared are considered together, the C_{26} carbon content appears the more preferable, but as the modern view of the formula of cholesterol and the interpretation given to the many derivatives obtained from it by oxidation is based on the work referred to, it seemed to us desirable to submit the question to a further test.

Harries has shown (*Annalen*, 1906, **343**, 311) that unsaturated alcohols, when submitted to the action of ozone, combine with one molecule of ozone to form ozonides, whilst unsaturated ketones absorb four atoms of oxygen, namely, three at the ethylene linking and one at the carbonyl group. These ozonides on treatment with water decompose as follows:



$$\begin{matrix}X{:}C\\ \|\\ Y{:}C\end{matrix} \longrightarrow \begin{matrix}X{:}C{\cdot}O\\ |\\ Y{:}C{\cdot}O\end{matrix}{>}O \longrightarrow X{:}CO + Y{:}CO + H_2O_2,$$

aldehydes or ketones and hydrogen peroxide being formed. If Windaus's formula is correct, cholestenone should absorb four atoms of oxygen under the influence of ozone, and the ozonide formed should react with water in the following way:



These aldehydes would be at once oxidised by the hydrogen peroxide, and we should expect to find among the final products a C_{26} acid and probably either formic or carbonic acid derived from the formaldehyde.

The action takes place broadly on the lines predicted, and we obtained as chief products the C_{26} ketonic acid described by Windaus, and carbon dioxide. Cholesterol, on similar treatment, formed an ozonide which also gave carbon dioxide on decomposition.

EXPERIMENTAL.

Ozonide of Cholestenone.—Ten grams of cholestenone were dissolved in 200 c.c. of dry chloroform, and a slow current of ozonised oxygen was bubbled through the solution until the ozone ceased to be absorbed and escaped freely. The chloroform was allowed to evaporate spontaneously, and the viscid oil left behind was dissolved in the least quantity of ethyl acetate and poured into a large excess of light petroleum. A considerable proportion of the ozonide separated in a soft, resinous form, which was again dissolved and reprecipitated. The substance was placed in a vacuum desiccator and finally obtained as a colourless, glassy solid which was readily powdered. Two different preparations on analysis gave the following figures:

I. 0·1767 gave 0·4224 CO_2 and 0·1458 H_2O. $C = 65{\cdot}29$; $H = 9{\cdot}17$.
II. 0·1781 ,, 0·4424 CO_2 ,, 0·1459 H_2O. $C = 67{\cdot}75$; $H = 9{\cdot}10$.
$C_{27}H_{44}O{\cdot}O_6$ requires $C = 67{\cdot}50$; $H = 9{\cdot}17$.
$C_{27}H_{44}O{\cdot}O_7$,, $C = 65{\cdot}40$; $H = 8{\cdot}87$ per cent.

These results seem to show that six or seven oxygen atoms are absorbed by the cholestenone molecule. We should have expected four atoms to be added in the case of a singly unsaturated ketone. It may be, however, that cholestenone contains a second ethylene linking which is not rendered apparent by the usual reagents.

Decomposition of the Ozonide by Water.—It was not, for subsequent experiments, found necessary to prepare the pure ozonide as above. Instead, the chloroform solution of the ozonide was mixed with about twenty times its volume of water and heated on the water-bath in a current of purified oxygen. The gases evolved were passed through measured quantities of standard baryta solution. The action was slow, the evolution of carbon dioxide continuing for many hours. The aqueous liquid remaining in the flask was milky, acid to litmus, and had a peculiar odour of orange oil which we have previously noticed in the course of some experiments on the oxidation of cholesterol with hydrogen peroxide. The solid product was left as a brown oil, which, on cooling, solidified to a brittle mass. This was dissolved in ether and the ethereal solution shaken with sodium carbonate to separate the acid products from unchanged cholestenone or other neutral substances.

The alkaline liquors were acidified when the acids separated in a thick clot. This, after drying, was extracted with light petroleum, which removed some oily, non-crystalline material and left the main product of the reaction in the form of a white powder, the yield being 25 per cent. of the original cholestenone. It was purified by recrystallisation from acetone and from a mixture of light petroleum and benzene, and was obtained from the latter solvent in leaves which melted at 155°:

0·2179 gave 0·6154 CO_2 and 0·2082 H_2O. $C = 77{\cdot}02$; $H = 10{\cdot}62$.
$C_{26}H_{42}O_3$ requires $C = 77{\cdot}55$; $H = 10{\cdot}52$ per cent.

The quantity of carbon dioxide evolved in these experiments was always very much less than would correspond with the oxidation of a terminal CH_2 group to carbon dioxide. Thus 0·6745 of pure ozonide gave 0·00649 of carbon dioxide, or about 1 per cent., whilst theory requires 9·8 per cent. In other experiments also the quantity obtained was about one-tenth part of that theoretically required. It seemed likely that this was due to the preferential oxidation of the C_{26} aldehydic substance, presumably formed, by the hydrogen peroxide. To test this we decomposed the crude product obtained by ozonising 10 grams of cholestenone, in the presence of very dilute hydrogen peroxide and sulphuric acid. The yield of carbon dioxide now obtained agreed very well with the explanation above suggested.

0·268 Gram of carbon dioxide was obtained together with 2·30 grams of the acid $C_{26}H_{42}O_3$. The quantity of carbon dioxide theoretically produced with this quantity of acid is 0·245 gram. The neutral products of the reaction contained a considerable quantity of unchanged cholestenone.

Identification of the Acid $C_{26}H_{42}O_3$.—The acid obtained by us agrees in all its properties with that obtained by Windaus by the oxidation of cholestenone with permanganate. On titration:

0·2571 required 6·37 c.c. *N*/10 sodium hydroxide. Equivalent = 403.
$C_{26}H_{42}O_3$, monobasic, requires 402.

The *oxime* was prepared according to the directions given by Windaus, and was obtained from ethyl acetate in needles which melted and decomposed at 191°:

0·1794 gave 0·4928 CO_2 and 0·1802 H_2O. C = 74·86; H = 11·16.
$C_{26}H_{43}O_3N$ requires C = 74·75; H = 10·38 per cent.

This acid formed a beautifully crystalline *potassium* salt.

On oxidising the keto-acid with potassium hypobromite, an acid was obtained which after crystallisation from benzene sintered at 127° and melted at 130° with gas evolution. It was deliquescent. On titration:

0·2240 required 14·0 c.c. *N*/10 sodium hydroxide. Equivalent = 160.
$C_{26}H_{42}O_6$, tribasic, requires 150.

The keto-acid therefore on further oxidation gives the tricarboxylic acid $C_{26}H_{42}O_6$.

In all these particulars our acid corresponded with the ketomonocarboxylic acid described by Windaus.

Action of Ozone on Cholesterol.—Ten grams of anhydrous cholesterol were ozonised in chloroform solution as described above. The product was purified by solution in ethyl acetate and precipitation with light petroleum. It dried in a vacuum to a perfectly transparent glass which readily powdered. It had all the properties of an ozonide. When heated on platinum it enflamed, and it liberated iodine from potassium iodide solution:

0·1796 gave 0·4896 CO_2 and 0·1687 H_2O. C = 74·35 ; H = 10·44.
$C_{27}H_{46}O \cdot O_3$ requires C = 74·66 ; H = 10·59 per cent.

It thus appears that the ozonide is formed by the addition of three atoms of oxygen at the ethylene linking of the alcohol in the normal manner.

Rotation.—0·9647 gram made up to 25 c.c. with chloroform gave α + 1·12° in a 2-dcm. tube; hence $[\alpha]_D^{20}$ + 14·51°. The rotation of cholesterol is $[\alpha]_D^{20}$ − 36°.

On treatment with water in a manner similar to that described under cholestenone, the aqueous distillate had an odour of orange oil, was acid, and after neutralisation and evaporation gave a little solid matter which strongly reduced ammoniacal silver solution and probably consisted of barium formate. In the absorption vessels containing the baryta a copious precipitate of barium carbonate was formed, which was collected and identified in the usual way. The water remaining in the flask was milky. It was acid, and gave the magenta test for aldehydes. The solid left was a brown resin, which dissolved in alkalis and gave precipitates with salts of the heavy metals. We have, however, not as yet been able to separate any of the constituents in a state of purity, but we are carrying out other experiments on derivatives of cholesterol which we hope will throw some light on these compounds.

Conclusions.

These experiments on cholestenone fully confirm the hypothesis of Windaus that this ketone contains an unsaturated side-chain with the double link in a vinyl group. If the relationship of cholestenone to cholesterol is that of a simple ketone to its secondary alcohol, then the latter substance must contain a similar unsaturated side-chain. This is confirmed by our observation that cholesterol forms an ozonide, which on decomposition with water yields carbon dioxide. Direct experimental proof of this point has hitherto been lacking if we except the somewhat complex reduction of cholestenone to cholesterol through an isomeric β-cholesterol, recently carried out by Diels and Linn (*Ber.*, 1908, **41**, 260).

The expenses of this work have been defrayed by a grant from the Royal Society, for which we take this opportunity of expressing our thanks.

PHYSIOLOGICAL LABORATORY,
UNIVERSITY OF LONDON.

Chem. Lab.
54 0.5

No. DLIV.] 1908.

cribers are respectfully rer

scriptions for 1909 are no

HE C Y

JAN 14

CONTAINING

PAPERS COMMUNICATED TO THE SOCIETY,

AND

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN OTHER JOURNALS.

VOLS. XCIII & XCIV.

Committee of Publication:

E. C. C. Baly.
Horace T. Brown, LL.D., F.R.S.
A. W. Crossley, D.Sc., Ph.D., F.R.S.
Wyndham R. Dunstan, M.A., F.R.S.
M. O. Forster, D.Sc., Ph.D., F.R.S.
J. T. Hewitt, M.A., D.Sc., Ph.D.
R. Meldola, F.R.S.
G. T. Morgan, D.Sc.
Sir W. Ramsay, K.C.B., LL.D., F.R.S.
A. Scott, M.A., D.Sc., F.R.S.
T. E. Thorpe, C.B., LL.D., F.R.S.
John Wade, D.Sc.

Editor:

J. C. Cain, D.Sc., Ph.D.

Sub-editor:

A. J. Greenaway.

Assistant Sub-editor:

C. H. Desch, D.Sc., Ph.D.

Abstractors:

E. F. Armstrong, Ph.D., D.Sc.
G. Barger, M.A., D.Sc.
R. J. Caldwell, D.Sc.
W. A. Davis, B.Sc.
H. M. Dawson, D.Sc., Ph.D.
T. Ewan, B.Sc., Ph.D.
J. V. Eyre, Ph.D.
W. H. Glover, Ph.D.
E. Goulding, D.Sc.
P. Haas, D.Sc., Ph.D.
W. D. Halliburton, M.D., F.R.S.
T. A. Henry, D.Sc.
E. Horton, B.Sc.
L. De Koningh.
Z. Kahan, B.Sc.
N. H. J. Miller, Ph.D.
G. T. Morgan, D.Sc.
J. C. Philip, M.A., Ph.D.
T. H. Pope, B.Sc.
W. Robertson.
E. J. Russell, D.Sc.
S. B. Schryver, D.Sc., Ph.D.
G. Senter, Ph.D., B.Sc.
W. P. Skertchly.
C. Smith, D.Sc.
L. J. Spencer, M.A.
J. J. Sudborough, Ph.D., D.Sc.
A. Jamieson Walker, Ph.D., B.A.
M. A. Whiteley, D.Sc.
W. O. Wootton, B.Sc.
G. Young, Ph.D.

LONDON:
GURNEY AND JACKSON (Successors to J. Van Voorst),
10 PATERNOSTER ROW.

R. CLAY AND SONS, LTD., BREAD ST. HILL, E.C., AND BUNGAY, SUFFOLK.

by Google

LIBRARY.

The Library is open for consultation and for the issue and return of books daily f[illegible].M. to 6 P.M. (Saturdays 10 A.M. to 2 P.M.), and in the evenin[illegible] those days on which the Chemical Society meets.

PUBLICATIONS OF THE SOCIETY.

With the exception of certain numbers of the Journals and Proceedings which are out of print, the following publications may be obtained from Messrs. Gurney and Jackson, 10, Paternoster Row, E.C.

		Price to Fellows.			Price to Public.		
		£	s.	d.	£	s.	d.
Memoirs and Proceedings, 1841—1847 (3 Vols.) ...	per vol.	1	0	0	1	10	0
Quarterly Journal, 1848—1862 (14 Vols.)	per vol.	1	0	0	1	10	0
,, ,, ,, ,, (Single Parts)	per part		5	0		7	6
Journal, 1862—1895	per vol.	1	10	0	1	10	0
,, ,, ,, (Single Parts)	per part		2	6		2	6
,, 1896 to present date	per vol.	2	0	0	2	0	0
,, ,, ,, (Single Parts)	per part		3	6		3	6
Proceedings, 1885 to present date	per vol.		7	6		7	6
,, ,, ,, (Single Parts) ...	per part			6			6
Annual Reports on the Progress of Chemistry (bound in cloth), Vols. I (1904), II (1905), III (1906), IV (1907)	per vol.		4	6		4	6
Collective Index, Vol. I. 1841—1872	per vol.		4	0		4	0
* ,, ,, ,, II. 1873—1882	per vol.		10	0		15	0
* ,, ,, ,, III. 1883—1892	per vol.		15	0	1	0	0
* ,, ,, ,, IV. 1893—1902	per vol.	1	0	0	1	10	0
†Jubilee Volume, 1891..			6	0		6	0
†Memorial Lectures, 1893—1900			7	6		7	6
†Library Catalogue, 1886			1	0		1	0
† ,, ,, 1903			2	6		2	6
†Cases for binding the Journal in 4 vols.	per year		4	0		4	0
Tables of International Atomic Weights (as recommended by the International Atomic Weights Committee) 1*s.* 6*d.* per dozen ; 12*s.* per hundred.							

* *Postage to Fellows One Shilling extra.*
† *Post free to Fellows.*

The Journal, which is published on the last day of each month, includes the Transactions of the Chemical Society and Abstracts of chemical papers published in other Journals.

The Proceedings contain certain papers read at the meetings and abstracts of the remainder and of the discussions. They are, as a rule, issued to the Fellows about a week after each Ordinary Meeting.

The Annual Reports on the Progress of Chemistry contain an epitome of the principal definite steps in advance which have been made during the year. Fellows can obtain, from the Assistant Secretary, cases for binding the Annual Reports, price One Shilling each.

Officers and Council.

Elected March 26, 1908.

PRESIDENT.

SIR WILLIAM RAMSAY, K.C.B., LL.D., F.R.S.

VICE-PRESIDENTS

WHO HAVE FILLED THE OFFICE OF PRESIDENT.

H. E. ARMSTRONG, Ph.D., LL.D., F.R.S.
A. CRUM BROWN, D.Sc., LL.D., F.R.S.
SIR WILLIAM CROOKES, D.Sc., F.R.S.
SIR JAMES DEWAR, M.A., LL.D., F.R.S.
A. G. VERNON HARCOURT, D.Sc., F.R.S.
RAPHAEL MELDOLA, F.R.S.
HUGO MÜLLER, Ph.D., LL.D., F.R.S.
W. ODLING, M.A., M.B., F.R.S.
J. EMERSON REYNOLDS, Sc.D., F.R.S.
SIR HENRY E. ROSCOE, LL.D., F.R.S.
W. J. RUSSELL, Ph.D., F.R.S.
T. E. THORPE, C.B., LL.D., F.R.S.
W. A. TILDEN, D.Sc., F.R.S.

VICE-PRESIDENTS.

J. CAMPBELL BROWN, D.Sc., LL.D.
J. J. DOBBIE, M.A., D.Sc., F.R.S.
F. STANLEY KIPPING, D.Sc., Ph.D., F.R.S.
RUDOLPH MESSEL, Ph.D.
SIR ALEXANDER PEDLER, C.I.E., F.R.S.
W. H. PERKIN, Ph.D., F.R.S.

TREASURER.

ALEXANDER SCOTT, M.A., D.Sc., F.R.S.

SECRETARIES.

M. O. FORSTER, D.Sc., Ph.D., F.R.S.
A. W. CROSSLEY, D.Sc., Ph.D., F.R.S.

FOREIGN SECRETARY.

HORACE T. BROWN, LL.D., F.R.S.

ORDINARY MEMBERS OF COUNCIL.

JULIAN L. BAKER.
G. T. BEILBY, F.R.S.
ALFRED C. CHAPMAN.
JULIUS B. COHEN, Ph.D., B.Sc.
J. T. HEWITT, M.A., D.Sc., Ph.D.
W. R. E. HODGKINSON, Ph.D.
H. A. D. JOWETT, D.Sc.
H. R. LE SUEUR, D.Sc.
F. E. MATTHEWS, Ph.D.
A. G. PERKIN, F.R.S.
W. J. SELL, M.A., Sc.D., F.R.S.
JOHN WADE, D.Sc.

ASSISTANT SECRETARY.

S. E. CARR.

LIBRARIAN.

F. W. CLIFFORD.

IMPORTANT NOTICES.

NOTICES TO AUTHORS OF PAPERS.

All communications for the Journal and for the Proceedings of the Society should be addressed to "The Secretaries, Chemical Society, Burlington House, W."

The attention of authors is directed to the following resolutions of the Council.

"No communication shall be included in the list of titles of papers to be brought before a Meeting of the Society, unless it is in the hands of the Secretaries **at least three days** before the date of the Meeting; and no announcement of titles can be made in the Proceedings until the communications have been received by the Secretaries."

"Papers which, on the report of referees, are deemed by the Council unsuitable for publication in the Transactions, shall be deposited in the Society's Archives." Authors are therefore advised to retain copies of their papers.

In all cases, an abstract of the paper, not exceeding three hundred words in length, should be supplied for insertion in the Proceedings. Communications are put down on the list for reading in the order in which they are received.

Authors are requested to write on their papers and abstracts the **address to which they wish proofs to be sent**, also to send their corrected proofs without delay to the **Editor, 28, Pembury Road, Clapton, N.E.**, *and not to the Printers.* If authors require more than the **50 copies** allowed by the Society, they should inform the Editor at the time they send in their corrected proofs, when the extra copies will be supplied at cost price.

It has been resolved by the Council that communications made to the Society which have **already appeared in any Foreign Journal** shall not be published in the Society's Transactions, unless this course is **specially recommended** by the Publication Committee, and this recommendation approved by the Council.

ILLUSTRATIONS, AND PLATES OF CURVES.

As the Illustrations for the Journal (including curves) are, as far as possible, executed in photographic "process" work, the drawings, &c., accompanying the papers **must be drawn carefully on a scale about twice the size of the finished block, on smooth white Bristol board in Indian ink, so as to admit of the blocks being prepared directly from the drawings.** Any lettering on these drawings should be of such a size that it will be clearly legible when reduced.

When it is necessary to employ **Plates**, these must be also of convenient dimensions.

Information as to **Illustrations** and the dimensions of **Plates** can be obtained on application to the Editor.

Abstractors are requested to send their MSS. and corrected proofs to the **Sub-editor**, The Orchard, Chertsey, Surrey, and to communicate change of address to the **Printers** (Messrs. Richard Clay and Sons, Limited, 8, Bread Street Hill, E.C.), as well as to the **Editors**.

BOUND IN LIBRARY
JUN 24 1909

3 9015 06512 1025
UNIVERSITY OF MICHIGAN